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TABLE OF CONTENTS

	Page	Russ. page
1. Oscillographic Polarography. Ya. P. Gokhshtein and Yu. A. Surkov	355	319
2. A Flame-Photoelectric Method for the Determination of Calcium in Solution. D. I. Ivanov	383	344
3. Quantitative Colorimetric Determination of Aliphatic Alcohols in the Ultraviolet. S. A. Shchukarev, S. N. Andreev, and I. A. Ostrovskaya	393	354
4. Quantitative Micro Determination of Carbon, in Particular in Tantalum Carbide. V. I. Smirnova and B. F. Ormont	399	359
5. An Apparatus for the Quantitative Absorption of Gases. B. F. Ormont and V. I. Smirnova	405	364
6. Polarographic Determination of Nitrates and Nitrites in Salts and Brines used for Meat Pickling. R. Pletikha and E. Krzhishova	407	366
7. A Study of the Errors Involved in the Chemical Analysis of Steels and Casts. A. B. Shaevich	415	373
Criticism		
8. The Analytical Chemistry of Bismuth. A. I. Busev. (A review)	419	377
Chronicle		
9. Dmitrii Ivanovich Ryabchikov (on his fiftieth birthday)	423	379
10. Ninth Conference on Spectroscopy	427	382

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OSCILLOGRAPHIC POLAROGRAPHY

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In recent years a new technique has been developed in polarographic analysis, in which an oscillograph is used for recording the polarographic currents. The method which has developed along this new direction has been called oscillographic polarography. With the development of oscillographic polarography even greater possibilities have been opened up to the technique of polarography; many processes which occur at high speed on the dropping mercury electrode are now within the scope of study, while it has become possible to determine electrode reaction rates and their reversibility.

Oscillographic polarography permits determination of the charging point during the growth of a drop and the capacity of the double electrical layer on the boundary of separation, mercury-solution. These are possible as a result of the recording on the cathode ray screens of oscillographic curves which reflect the processes occurring on the dropping mercury electrode during rapid potential changes on the electrodes of the polarographic cell.

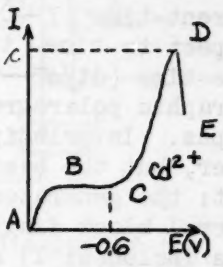

Fig. 1. Oscillograph curve for cadmium.

The principle of the method is simple: a voltage which is proportional to that applied to the polarographic cell is applied to the plate which deflects the cathode ray of the oscillograph in a horizontal direction, while a voltage proportional to the current flowing through the electrolytic cell is applied to the plate deflecting the cathode ray in a vertical direction. A current-voltage curve is thereby obtained on the screen. When a saw-toothed voltage is applied to the cell electrodes, the form of the curves is that shown in Fig. 1. It is possible to determine what particular element is in solution from the value of the voltage at which there is a sudden increase in current flowing through the cell (Point C). A further increase in voltage across the cell after passing the reduction potential (or oxidation potential) for a particular substance leads to an increase in the current flowing through the cell to some definite maximum value. From the maximum value for the current (Point G) it is possible to determine the amount of test material in solution.

Some of the apparatus described below permit determinations to be made to an accuracy of up to 1%. Measurement of currents of the order of 10^{-2} μA means that micro determinations can be carried out.

First and second order maxima /1/, which interfere with quantitative analysis, appear on the current-voltage curves when using conventional polarography. In order to suppress these maxima the technique usually employed is to add surface active agents; these however tend to inhibit the electrochemical processes and give rise to " spurious" polarographic curves /2/. Maxima are absent in oscillographic polarography because the surface of the mercury drop is stationary while one impulse is being applied. There is therefore no need to add surface active agents when this technique is used.

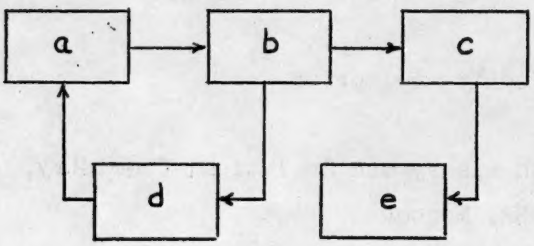

Fig. 2 Block Scheme of an Oscillographic Polarograph
a) Generator, b) polarographic cell, c) current or voltage amplifier, d) synchronizing system, e) oscillograph

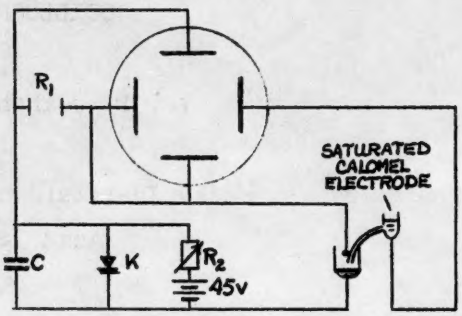

Fig. 3. Matheson and Nichol's Oscillographic Polarograph.

The type of oscillographic curve obtained depends on the set-up used; thus the following types of curves have been obtained by various authors: current-time (I—t), potential-time (E—t), differential-of-voltage-with respect-to-time- time (dE/dt—t), differential of current with respect to time-time (dI/dT—t). Nearly every one of the papers published on oscillographic polarography contains details of original oscillographic polarographs. In principle all the various set-ups differ very little from each other, but the basic set-up determines the potentialities of the instrument: the generator, the amplifier, and various synchronizing systems. A general block diagram of an oscillographic polarograph is shown in Fig. 2. This includes: 1) a generator of impulses of definite shape, amplitude, frequency, and duration; 2) the polarographic cell (with possibly a calomel electrode); 3) an amplifier for current or voltage according to the frequency of the impulses applied to the cell; 4) a synchronizing system, designed for synchronizing the frequency of the impulses applied to the cell with the drop time of the electrode; 5) a normal oscilloscope or a specially constructed oscilloscope designed for reproducing oscillographic curves. Recording on the screen is usually photographic (possibly even visually).

I. Original Blocks (Circuits) for Oscillographic Polarographs.

In this review we have considered it expedient only to discuss the most interesting and original blocks (circuits) published for the construction of oscillographic polarographs. The radiotechnical schemes adduced below are simplified variants of the original circuits proposed by the authors of the articles discussed.

Matheson and Nichols /3/ were apparently the first to get the idea of using a cathode ray tube in polarography. They were attracted by the convenience and rapidity with which oscillographic curves of I—E could be registered by this new technique. They used an alternating sinusoidal voltage from a circuit with an amplitude of 1.5 V on top of a constant voltage of 1.5 V.

Thus a change in potential of from 0 to 3 occurs at a frequency of 60 c.p. The current flowing through the cell on passing through an external resistance causes a drop in potential across the resistor which is then applied after amplification to the vertical plates of the oscillograph. The vertical deflection of the cathode ray is proportional to the current flowing through the cell.

The ray is swept horizontally by means of a sinusoidal voltage of the same frequency. A current-voltage curve is accordingly obtained on the screen. Reproduction of the oscillogram is achieved by synchronizing drop time with sweep frequency (60 drops/sec.).

Another variant was suggested by the same authors in which a linearly increasing voltage of 0 – 2.4 V was applied to the cell; this was supplied from a condenser charging through a variable resistance from a battery. The voltage was applied periodically by closing the condenser 30 times a second by means of an electric motor (Fig. 3).

Matheson and Nichols obtained a current-voltage curve of the type shown in Fig. 4 in which the drop time of 1/30 sec.; was accurately synchronized with voltage impulses of 30 cycles per second. When this method is used only one trace per drop is obtained and the current-voltage curve obtained on the visible screen is in the form of a stationary image.

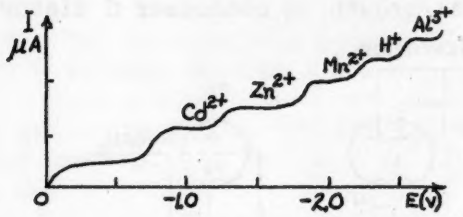

Fig. 4. Oscillogram for 0.1 N LiCl containing Cd^{2+}, Zn^{2+}, Mn^{2+}, Al^{3+}

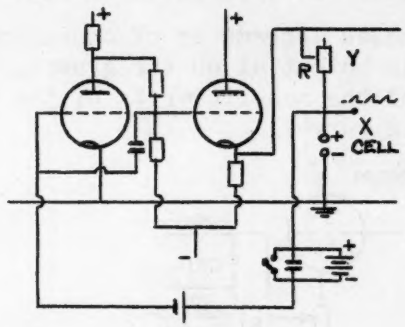

Fig.5 Schematic diagram of the Randles Generator

The authors found that the I – E curve was very similar to the current-voltage curves obtained by means of the ordinary method but the diffusion durrent was not strictly proportional to concentration. The half-wave potentials on Fig. 4 are slightly more negative than those obtained when using ordinary polarography.

This work despite its limitation is of interest because it demonstrated the possibility of using the oscillograph for polarographic studies. Matheson and Nichol's work showed that a change in potential drop on the load resistance has an essential effect on the nature of the curves.

Much later, Randles [4], proposed a new set-up in which this snag was eliminated and in which considerable improvements were made in the oscillographic method.

In set-ups constructed on the basis of the system suggested by Matheson and Nichols the error in the measured values of the current is determined by the ratio R/R_i (where R is the load resistance, R_i – the internal cell resistance) and increases with the latter.

A simplified Randles set-up is depicted in Fig. 5.

In such a system any change in the potential drop across the load resistor R alters the potential differences applied to the cell by 0.5% of the value of the change in the potential drop across R. This is achieved by using a cathode repeater with a return communication. The potential across the polarographic cell is supplied from a condenser C charging through a variable resistance from a battery. The frequency of the voltage change is altered step-wise by varying the resistance through which the condenser is charged. In this way a rate of potential increase across the cell of 0.14 to 0.88 V/sec can be obtained.

The increase in potential applied to the cell is synchronized with the fall of a drop and started after a given time interval (0.5-7 sec) after the fall of a drop. Such a delay in applying the potential permits an I– E curve to be recorded for any size of drop. This is ensured by incorporating in one of the anodes a univibrator relay which, at the fall of a drop, short-circuits a condenser C during the delay time and opens it for the time during which the potential applied to the cell increases. Delay time is regulated by changing RC in the univibrator circuit and corresponds to the duration of its impulse. If it is necessary to take several I – E curves corresponding to various drop sizes, then the univibrator is changed over for a multi-vibrator. To record weak currents passing through the cell on the screen a current amplifier is used which has variable amplification. The current voltage curve is of the type shown in Fig. 1.

Randles' scheme is of considerable interest although such a slow increase in potential on the growing drop (a tenth of the growing period of the drop) and the non-linearity of the potential growth on condenser C distort the I – E curve.

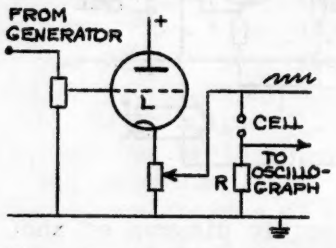

Fig. 6. The Delahay scheme (I)

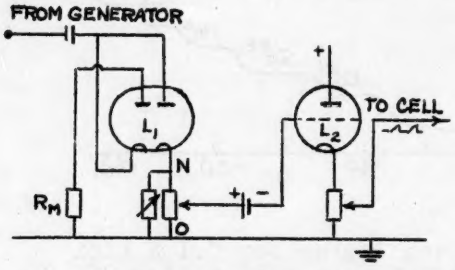

Fig. 7. The Delahay scheme (II).

These drawbacks were overcome a little later by Delahay [5]. Delahay got oscillographic curves of I – E by applying a saw-tooth voltage to a cell with a load resistor R. A simple generator operating on a thyratron was used to get the saw-tooth voltage. The saw-tooth voltage from the generator is applied through a divider (potentiometer) to the current amplifier, from the cathode of which the voltage of required amplitude and frequency is applied to the cell (Fig. 6).

The potential drop across a resistance R connected in series with the cell provides the polarographic current I to be recorded. This potential drop IR is amplified and applied to the vertical plates of the oscillograph. The vertical displacement of the ray is accordingly proportional to the current recorded. The horizontal displacement of the ray is proportional to the voltage applied to the cell; the horizontal sweep of the cathode ray is produced by directly applying a saw-tooth voltage of 160-180 V from the generator to the horizontal plates of the oscillograph. In this set-up therefore, the constant voltage applied to the cell is regulated as well as the voltage frequency and amplitude. The rate at which the potential applied to the cell increases can be as high as 100 V/sec. With such a high rate of potential increase it is

possible to record I–E curves corresponding to different drop sizes and to follow certain rapidly occurring electrode processes.

The drawback of this scheme is that the next voltage increase applied to the cell starts immediately after the sudden drop of the preceding impulse, i.e., at a moment when the ions reduced on the dropping mercury electrode have not succeeded in being completely oxidized and diffuse back into solution. This effect leads to a decrease in the maximum current from its true value particularly at the beginning of the oscillographic curve (i.e. for low cell voltages).

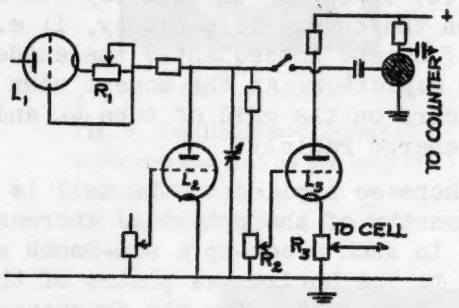

Fig. 8. The G. E. O. Kh. I. Oscillographic Polarograph

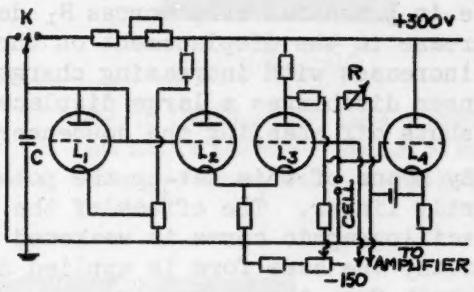

Fig. 11. Snowden and Page's Oscillographic Polarograph

In order to eliminate this snag Delahay [6], suggested another variant whereby a voltage impulse could be applied to the cell after a given time interval. Such a scheme permits ions reduced on the dropping mercury cathode by the preceding impulse to diffuse back again into solution up to the time when the next impulse is applied. In this set-up the rate of potential increase was increased to 1000 V/sec. This is achieved by chopping the base of the saw-tooth impulses with a double diode (Fig. 7). The apices of the saw-tooth impulses are applied to the voltage amplifier, from the cathode of which impulses of the requisite duration and amplitude are applied to the cell as before. The shape of the voltage depends on the value of the ratio R_M/R_{NO}. At $R_M/R_{NO} = 1$, the duration of a saw-tooth impulse is equal to the interval between them. For $R_M = 0$, this set-up gives the usual saw-tooth wave and operates like the previous set-up. Both set-ups permit several waves to be photographed during the time of growth of one drop; these waves give a complete picture of of the processes occurring on the growing drop.

The set-up which the authors of the present review [7], constructed is a modified Delahay circuit; by means of our apparatus it is possible to carry out quantitative determinations for the same rate of change of the saw-tooth voltage (Fig. 8).

The circuit is composed of several cascades with varying functions: 1) a saw-tooth voltage generator; 2) an amplifier for the saw-tooth voltage applied to the electrolytic cell; 3) an amplifier for the current flowing through the polarographic cell; 4) a source of supply (for anode voltage and filament heating); 5) a mechanical counter for recording the number of sweeps per unit time.

A generator based on a thyratron was used as a saw-tooth voltage supply; a variable capacitor and high resistance were coupled in parallel with this generator.

The capacitor was charged through tube L_1 which gives rise to an increasing

voltage on the thyratron anode. When the voltage on the thyratron anode reaches a value such that it fires, the capacitor discharges instantaneously almost to zero through it.

The process then starts all over again. A saw-tooth voltage with an amplitude of ca. 200 V is therefore obtained on the condenser. From a potentiometer connected in parallel to the capacitor, a saw-tooth voltage is applied to the voltage amplifier; from its cathode, impulses of the requisite value pass on to the cell.

To improve the linearity of the voltage a tube L_1 with a reverse connection with respect to the current (cathode-grid) is used. In this way the decrease in potential drop across R_1 depends on the change in capacity, i. e. on a decrease in the displacement on the grid of L_1, and consequently the anode current increases with increasing charge on the capacitor. At the moment when the condenser discharges a large displacement occurs on the grid of tube L_1 and the tube shuts off, enabling the condenser to discharge rapidly.

By means of this set-up the potential increase applied to the cell is satisfactorily linear. The effect of the non-linearity of the potential increase on the oscillographic curve is weakened because in such a set-up a saw-tooth wave of exactly the same form is applied directly to the horizontal plates of the oscillograph from the generator. The possibilities of changing the frequency of the impulses applied to the cell up to 50 times/sec was provided for in the generator by including a potentiometer R_{10}. The generator permits a rate of potential increase of the cell of ca. 100 V/sec. In principle one could get a much higher rate of potential increase and consequently a greater sensitivity. In the actual set-up however the use of a saw-tooth voltage is a limiting factor. The presence of the amplifier L_3 in the first place means a low output resistance for the ganerator so that the effect of the current on the output voltage of the generator is reduced to a minimum, and secondly, permits the amplitude of the saw-tooth voltage applied to the cell to be regulated. In the given set-up the saw-tooth voltage from the amplifier L_3 is applied to the cell with a load resistor. The polarographic cell itself consists of a dropping mercury cathode and a calomel anode assembled separately and screened from electromagnetic fields. A screened resistance box of 100 kΩ serves as load resistor. Its value is changed according to the amplification required (this is determined by the concentration of test element in solution).

The general principles of how to get current-voltage curves are considered at the beginning of this article. Normally the current obtained in a polarographic cell is of the order of a few microamps while the potential drop it gives rise to across a load resistor is of the order of thousands or hundreds of microvolts. It is usually necessary therefore to amplify the voltage $10^4 - 10^5$ times so that the potential drop across the cell can be connected directly to the vertical plates of the oscillograph. A preamplifier is used in conjunction with the oscillograph for vertical amplification. The overall amplification of oscillograph plus preamplifier is sufficient for use with a half-inch tube. In order to eliminate the effect of the next increase in the saw-tooth voltage which begins immediately after the sudden drop of the previous impulse, on the maximum current, a synchronizing system is included so as to synchronize the frequency of the impulses applied to the cell with the drop time.

A mechanical impulse counter based on a non-incandescent thyratron – the MTKh-90, is used in this set-up for determining the rate of voltage change in the cell.

The whole apparatus is supplied from an electronically stabilized source and from accumulators.

Fig. 9. Oscillographic curves of cadmium and zinc on one drop of mercury during its growth: $\underline{m}$ = 2.6 mg/sec.; $\underline{t}$ = 3.6 sec.; α = 18 V/sec.

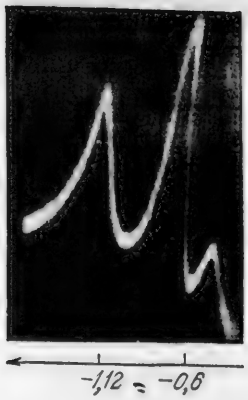

Fig. 10. Oscillographic curve of cadmium and zinc on one drop of mercury at maximal size: $\underline{m}$ = 2.6 mg/sec.; $\underline{t}$ = 3.6 sec.; α = 18 V/sec.

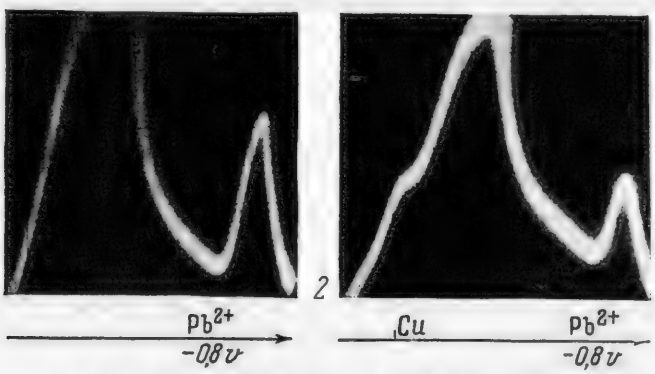

Fig. 21. Determination of lead in the presence of copper and zinc in 0.1 N KNO_3.

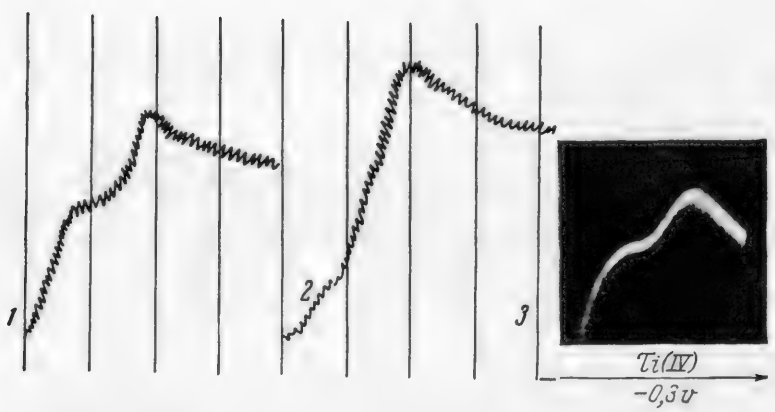

Fig. 22. Polarogramms and oscillogramm in the presence of iron and vanadium.

Figs. 9 and 10 represent oscillographic curves obtained for 10^{-4} M $CdCl_2$ and 10^{-4} M $ZnCl_2$ in 0.1 N KCl, using the oscillographic polarograph of the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry. Electrolysis was carried out using a saw-tooth voltage amplitude of −1.8 V relative to the saturated calomel electrode in the absence of dissolved atmospheric oxygen.

Fig. 9 contains a series of oscillographic curves obtained from one drop of mercury at various stages of its growth, while Fig. 10 was recorded for one drop of mercury at its maximum size during a few fractions of a second before it broke off.

From Fig. 10 it is evident that the oscillographic curves for cadmium and zinc ions appear at potentials of −1.12 and −0.6 V relative to the saturated calomel electrode. One of the most recent constructions described for an oscillographic polarograph which operates on the same principle (saw-tooth voltage) is that of Snowden and Page [8]. These authors give a detailed description of all the component circuits involved. It is built on the same principle as Randles' instrument but it also contains some original refinements; it consists of a generator, a compensator, a synchronizer (delay gate) and an amplifier with a cathode-ray tube. A clipped saw-tooth voltage is applied to the cell. The interval between impulses is 3-6 seconds. At the drop point the voltage impulse from a load resistor R is applied to a synchronizer which is an ordinary vibrator, one anode of which includes a relay with a key K (Fig. 11). The synchronizer is not shown in the diagram. When this is done the uni-vibrator is reversed and the relay is opened during the time the impulse is applied. After the uni-vibrator is returned to its original position (i.e. after 3-6 seconds) the relay is switched on again and the generator started. The generator is a condenser C which periodically charges through a variable resistance from the anode voltage. The apices of the saw-tooth voltage are clipped with a thyratron working as a diode. The amplitude of the clipped saw-tooth is regulated by changing the potential of the tube cathode. The impulse from the generator is applied to the generator and from the latter to the cell. The compensator thereby eliminates the effect of the load resistance on the current flowing through the cell. The change in potential drop across the load resistor is amplified by means of a current amplifier and is applied to the vertical plates of the oscillograph. The horizontal sweep is effected from the same saw-tooth generator. I − E curves are traced on the screen. Snowden and Page's polarograph is a more complex and more refined instrument than preceding ones and extends the boundaries of polarographic analysis.

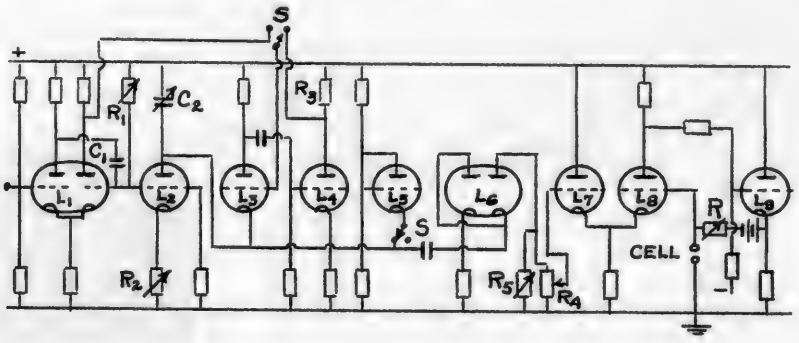

Fig. 12. Cruse and Heberle's Polarograph

Bearing in mind the drawbacks of methods involving saw-tooth voltages noted above, and those of impulse methods which complicate visual observation

for large drop times, Cruse and Heberle [9], used a more universal system than previous authors for their oscillographic studies.

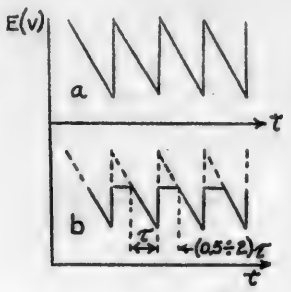

Fig. 13. Saw-tooth voltage (a), converted into impulses (b).

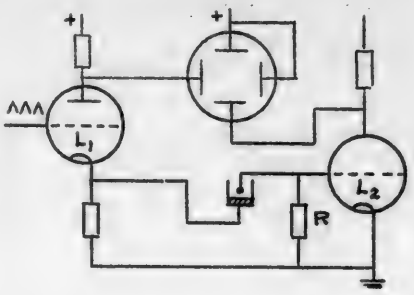

Fig. 14. Seveik's Set-up.

In Cruse and Heberle's polarograph either a saw-tooth voltage or impulses of a linearly increasing voltage with a given delay time can be applied to the polarographic cell. A simplified schematic diagram of their instrument is shown in Fig. 12.

Condenser C_2 is linearly charged through a pentode L_2 to the value of the potential drop across the resistor R_3 and is rapidly discharged on reversing the multivibrator which consists of L_2 and L_4, the cycle is then repeated. A saw-tooth voltage (Fig. 13 a) is thus obtained which is clipped by a diode L_6 and converted into impulses (Fig. 13, b), following each other at intervals 0.5 – 2 times the duration of the impulse itself. Their frequency is determined by the parameters R_2 and C_2, the amplitude by the position of the potentiometer R_4 and the interval between them by the value of R_5. When operating under impulse conditions the switch S is used for switching off the multivibrator L_3L_4 and switching on the univibrator L_1 and L_3. The univibrator is started by an impulse from the vertical amplifier at the moment of drop fall. Under these conditions the delay time of the impulse applied to the cell after drop fall is determined by the value of the circuit R_1C_1 and changes with changes in R_1. The diode switch L_5 is used for restricting the delayed impulses.

The impulses from the generator are applied to the cell through a compensator designed for eliminating the effect of the load resistor R on the current flowing through the cell.

Cruse and Heberle's polarograph permits both visual observation and qualitative determination (when using the saw-tooth voltage) as well as quantitative measurements and study of reaction kinetics to be made (under impulse conditions).

Seveik [10], used an original set-up for an oscillographic polarograph based on the use of a triangular sweep for investigating polarization phenomena. Getting I – E curves was again the basis of his method as in previous work. The new features in this case are the application of triangular impulses to the polarographic cell (Fig. 14). This type of voltage permits one to obtain simultaneously both cathode and anode waves on the polarogram and to make deductions as to the reversibility of a process according to their arrangement with respect to the ordinate. The triangular voltage is taken from the cathode of the output tube L_1 of the generator and applied to the polarographic cell fitted with a load resistor R. The potential drop across the load resistor is amplified by the current amplifier (represented by only one tube L_2) and applied to the vertical plates of the oscillograph. The horizontal sweep is also effected by means of the same triangular voltage taken from the

anode of the output valve L_1 of the generator. Thus on applying to the plates, which deflect the ray horizontally, a triangular voltage, there results a regular movement of the ray along the horizontal on both sides of it.

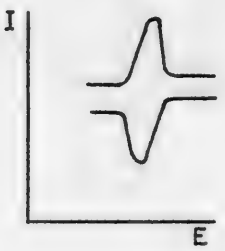

Fig. 15. Oscillogram for Lead taken at ν = 20.8 cycles /sec.

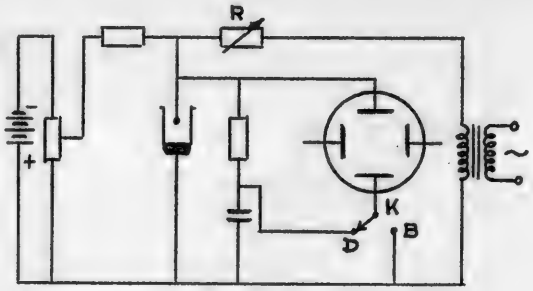

Fig. 16. The Heyrovsky Polarograph. (Schematic)

During the period of growth of the triangular voltage the ray moves from left to right and registers reduction processes (as in the previous set-ups); during the period when the triangular voltage is decreasing the ray moves in the opposite direction and registers oxidation processes. The amplitude of the triangular voltage on the cell was 2 V, frequency (1 – 100) cycles/sec.. Photographs were taken at the last moment of drop growth when the rate of increase of drop surface is very small and the polarographic current does not change.

Fig. 15 represents an oscillogram obtained for 10^{-4} M $Pb(NO_3)_2$ in 1 N NaOH, using Seveik's polarograph. From this graph it can be seen that the maximum current for the upper cathode wave which is caused by reduction of $HPbO_2$ on the dropping mercury electrode and the lower anode wave both appear at practically the same potential, thus testifying to the reversibility of these two electrode processes.

All the types of oscillographic polarographs considered above, independently of the concentration of test material in solution and the character of the investigation, in the final count boil down to recording of I – E curves. In this sense they represent one side of the development of oscillographic polarography along the lines of increasing the limits at which ions can be detected and determined in solution. Seveik's polarograph in addition permits determination of the reversibility of electrode reactions, two curves of I – E (cathode and anode waves) being obtained. There are some characteristic differences in the character of the oscillograms obtained by means of one of the earlier forms of polarographs used by Heyrovsky for establishing the reversibility and rate of electrode reactions [11].

Heyrovsky's polarograph (Fig. 16) gives oscillographic curves of potential against time (E – t) and of dE/dt – t. To do this a direct voltage from a battery and an alternating voltage from a transformer is applied to the cell, the alternating voltage is either of a sinusoidal form with a frequency of 50 cycles per second or in the form of square impulses from a generator. The value of the direct and alternating voltages is regulated potentiometrically. To establish the reversibility and the rate of electrode reactions a switch over to two positions can be effected by means of contact K (Fig. 16). Position KB gives E – t curves on the screen, while in position KD, dE/dt – t curves are obtained.

Fig. 17 represents a potential – time curve and its derivative, which were obtained on a Heyrovksy polarograph for a solution of 1 N NAOH containing $2 \cdot 10^{-3}$ N $Pb(NO_3)_2$. Two steps are visible on both the ascending and descending branches of the curve at the same values of the potential. On the ascending branch, the step is the result of the reduction of the biplumbite ion on the dropping mercury electrode, while the step on the descending branch is caused by oxidation of lead. On the $dE/dt - t$ curve, a depression is formed which corresponds to the steps on the $E - t$ curve. The height of the depression increases with concentration of depolarizers. Exact measurements are however out of the question with this type of polarograph, since the oscillographic curve grows and subsides with each mercury drop.

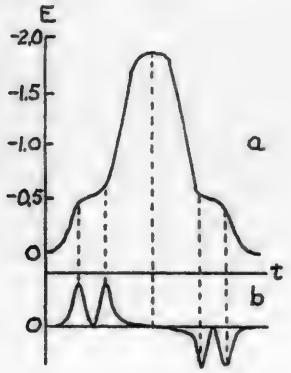

Fig. 17. An (E – t) curve (a), and the derivative curve (b).

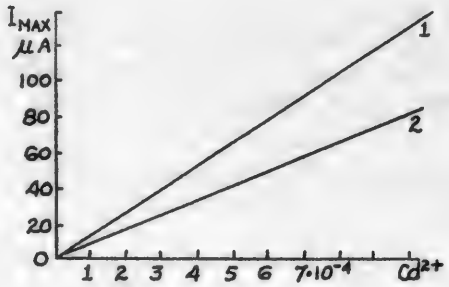

Fig. 18. Values of the Maximum Current for Various Cadmium Concentrations.
1 – Impulse method: 2 – saw-tooth method; Cd^{2+} in 0.1 M KCl; α = 12.5 V/sec; m = 0.835 mg/sec; t = 8.44 sec.

Details of this set-up of Heyrovsky's were published immediately after those of Matheson and Nichol's work, and despite the simplicity of its construction and operating principles it has considerably widened the scope of oscillographic polarography for analytical purposes. This set-up, however, had one serious defect – the difficulty of working out the results because of the non-linearity of potential increase with time.

II. Theoretical Equations.

A. The diffusion current on oscillographic curves.

1). Equations suggested. Fig. 1 represents an oscillographic curve for cadmium on which the section AB corresponds to the maximum capacity current while the part CDE corresponds to the diffusion current of Cd, and CD the maximal diffusion current. It has been established that there is a linear relation between maximum current and concentration of material in solution.

As in ordinary polarography, in deriving an equation for the limiting diffusion current, considerable attention has been paid in oscillographic polarography to deriving an equation for the maximum current (point D on the section CD of Fig. 1). It is only very recently that a new modification of the semi-empirical Ilkovich equation for the limiting diffusion current in ordinary polarography was suggested by Stackelberg [12], it is of the following form:

$$I_g = 619 n c D^{1/2} g^{2/3} t^{-1/2} (1 + 17 D^{1/2} g^{-1/3} t^{1/2}), \qquad (1)$$

where n is the number of electrons participating in a reaction; c is the concentration of material in millimols/ liter; D is the diffusion coefficient of the material in cm^2/sec; t is the drop time of the capillary and g = mt (m is the amount of mercury in mg flowing through the capillary per second.

If all the constants included in the equation are taken into account this modified Ilkovich equation can be changed into an equation which was derived by one of the authors of the present article [13]. Randles [14], and Seveik [10], independently derived equations for the maximum current of the oscillographic curve for the case where the electrode reaction is reversible and the reaction products are soluble in water.

Assuming that the rate of change of electrode potential relative to the solution is constant, Randles showed that

$$\frac{0.059}{n} \log (c_M^o/c_S^o) = \alpha(t - t_o), \qquad (2)$$

where c_M^o is the concentration of metal in the amalgam; c_S^o is the concentration of metal ions in the solution near the surface of the mercury drop; n is the number of electrons taking part in the reaction; α is the rate of change of potential in volts/ sec; t is the time in seconds relative to t_o, and t_o is the time at which $c_M^o = c_S^o$.

By assuming the concentration of the test ion in the bulk of the solution to be

$$c = c_S^o + \sqrt{\frac{D_M^o}{D_S}} \cdot c_M^o \qquad (3)$$

(D_M^o is the diffusion coefficient of metal in the amalgam, D_S is the diffusion coefficient of the ion in solution), and solving the equation for linear diffusion graphically [15], Randles found that

$$I_{max} = \frac{1.24\pi F \cdot c}{0.0118)^{1/2} \cdot 10^3} n^{3/2} \gamma^{2/3} t_{max}^{2/3} \alpha^{1/2} D^{1/2}, \qquad (4)$$

where I_{max} is the maximum value of the current of the oscillograph wave expressed in amperes; t_{max} is the time in the course of which I_{max} is attained; F is the Faraday number; γ is defined by the relation $r_o^3 = 3mt/4\pi d = \gamma t$, i.e., $\gamma = 3m/4\pi d$ (m is the amount of mercury in g issuing from the capillary/sec., d is the density of mercury, t is the drop time of the capillary, D is the diffusion coefficient of the reduced ion, and c is the ionic concentration expressed in mols/liter. The remaining legends in (4) are the same as in equation (2).

Substituting the numerical values in equation (4) we find that

$$I_{max} = 234.4 n^{3/2} \cdot m^{2/3} \cdot t_{max}^{2/3} \alpha^{1/2} \cdot D^{1/3} \cdot c \text{ amperes} \qquad (5)$$

where all the legends are the same as in equation (4). Using the linear diffusion equation and taking into account the boundary conditions of the electrolysis and introducing hyperbolic functions into a series of equations, Seveik derived the following equation for the maximum current of the oscillographic curve:

$$I_{max} = 0.0191 \cdot F n^{3/2} m^{2/3} t_{max}^{2/3} D^{1/2} \alpha^{1/2} c \text{ microamperes}$$

where m is expressed in mg/sec, while c is the concentration in millimols/ liter. The remaining legends are same as in equations (2) and (4).

It is not difficult to see that equations (2) and (4) are identical apart from the constant. The modified Ilkovich equation [Equation (1)] is externally similar to the equations of Randles and Seveik.

TABLE 1

Effect of Rate of Change of Potential on the Maximum Current of Cadmium

$1.039 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10^{-5}$ cm^2/sec; m = 0.835 mg/sec; t_{max} = 8.44 sec; h = 270 mm; experimental temperature 25° ± 0.1°.

$\alpha^{1/2}$, where α- is the rate of change of potential in V/sec.	Maximum Current of Reduced Ion			Difference in % between experimental values and those calculated by means of Seveik's equation	Difference in % between experimental values and those calculated by means of Randles' equation
	Found, in μA	Calculated from Seveik's equation, in μA	Calculated from Randles' equation, in μA		
1.686	3.97	7.39	9.39	46.27	60.62
2.016	4.79	8.83	11.23	45.72	57.31
2.363	5.73	10.33	13.14	44.50	56.37
2.509	5.95	11.47	14.21	46.73	58.13
2.649	6.54	12.03	15.30	45.60	57.23
2.795	6.51	12.14	15.44	46.42	57.89
3.006	7.50	13.65	17.35	45.07	56.79
3.536	8.38	16.05	20.41	47.79	58.95
$1.039 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10^{-5} cm^2/sec$.; m = 0.347 mg/sec.; t_{max} = 14.5 sec.; h = 270 mm					
1.820	3.75	6.45	8.21	41.84	54.34
2.492	6.17	8.83	11.24	30.07	45.07
2.547	6.39	9.24	11.75	30.77	45.58
2.882	7.72	10.44	13.29	26.21	41.92
3.077	9.48	11.16	13.88	15.03	31.69
3.544	11.02	12.85	15.99	14.20	31.06
3.625	11.03	12.86	16.36	14.23	32.58
3.751	11.69	13.60	16.93	14.05	30.96
4.156	12.57	14.72	18.75	14.60	32.95

2) Checking the Theoretical Equations of Randles and Seveik.

Randles [14], and Seveik [10], investigated the effect of the rate of potential change on the value of the maximum current of the reduced ion. The ratios of $I_{max}/\alpha^{1/2}$ were found to be approximately equal to the theoretical values.

Delahay [16], also studied the relation between maximum current and the square root of the rate of change of potential for cadmium, zinc, and nickel ions. Delahay plotted the values of I_{max} found, on the ordinate and corresponding values of $\alpha^{1/2}$ on the abscissa. The curves for cadmium are practically straight lines. For three concentrations of zinc(1; 0.5; 0.2 mM) it was found that at low rates of potential change the results relating I_{max} with $\alpha^{1/2}$ deviated only slightly from linearity, but at high values of the rate of potential change there was considerable deviation from linearity.

The maximum value of the current for 1, 0.5, and 0.2 mM of zinc calculated from equation (5) for $\alpha^{1/2}$ = 5.75 were found to be 258, 129, and 54 μA, respectively, while the corresponding experimental values for the same zinc concentrations were 56, 37, and 11 μA.

The percentage deviations between theory and experiment were 78, 71, and 80, respectively, which are considerably in excess of the 28% deviation of the theoretical values from the maximum current found by Randles at $\alpha^{1/2}$=0.51 V/sec.

In order to check on the equations of Randles and Seveik in more detail we carried out a number of tests on the study of the effect of the rate of change of potential on the maximum current of cadmium. 0.1 N KCl containing $1.039 \cdot 10^{-4}$ M $CdCl_2$ was electrolyzed in the absence of atmospheric oxygen for different rates of potential change. Electrolysis was carried out using two dropping mercury electrodes of differing drop time.

The mean values of the actual diffusion coefficient of Cd^{2+} determined by a diffraction method [17], were substituted in the equations of Randles and Seveik, respectively. The rate of change of potential applied to the cell depends on the frequency of the sweep generator (ν) and on the amplitude of the saw-tooth voltage ($E_\sim$). The product of these two factors gives the rate of change of the saw-tooth voltage (α) applied to the cell.

Experimental and calculated results are included in Table 1. The values of the maximum current correspond to the last instant of drop growth when the rate at which the surface of the drop increases becomes very small and the polarographic current hardly changes. For comparison, calculated values are taken as 100%. The calculated values of the maximum current for Cd adduced in Table 1 correspond to the case where the next increase in potential starts immediately after the sudden drop of the previous impulse. We call this method of applying the potential to the cell electrodes the saw-tooth method in contrast to the impulse method in which the impulse is applied to the electrolytic cell with some delay after the beginning of drop formation.

The results given in Table 1 show that the values of I_{max} calculated according to Randles' equation deviate to a considerably greater extent from the experimental values of the cadmium maximum current than those calculated according to Seveik's formula. The slower the drop rate the smaller the deviation between calculated and observed results. With increasing rate of potential change for a very slow drop time (14.5 sec.) the percentage deviation between the experimental results and those calculated by Seveik's equation rises to 14, while on further increasing α the deviation becomes practically constant. The values of the cadmium maximum current calculated according to Randles' equation differ from the $I_{max.}$ values calculated according to Seveik's equation by approximately 12 – 18%. This deviation between the values of I_{max} calculated by means of equations (5) and (6) can be explained by the fact that Randles solved the linear diffusion equation less accurately than Seveik. Moreover in deriving his equation for the maximum current Randles assumed that the concentration of test ion in solution is equal to its concentration near the mercury drop surface plus the product of the concentration of metal in the amalgam and the square root of the ratio of the diffusion coefficient of the metal in the amalgam to the diffusion coefficient of the ion in solution. These assumptions however are innaccurate, since diffusion conditions toward the dropping mercury electrode differ from the conditions assumed by Randles.

The passage of a current through an electrolytic cell can be regarded as a special case of a heterogeneous chemical transformation [18]. Like all heterogeneous transformations it consists of three stages: a) transfer of ions from the depth of the solution to the electrode surface, b) a particular electrochemical reaction (discharge of ions on the cathode or their formation on the anode), c) formation of reaction end products and their precipitation on the electrode surface. The system mercury electrode-metal ions represents a system in which the discharge products are removed in the case where the metal forms an amalgam with mercury. The discharged metal ions in the form of atoms dissolve in mercury [e. g. $Cd^{2+} + 2\,e + Hg \rightleftharpoons Cd(Hg)$] and are removed from the surface by agitation. The boundary, metal-solution, in the case considered is a membrane which is permeable to discharged particles.

In oscillographic polarography where the rate of potential increase applied

to the cell differs somewhat from the rates used in ordinary polarography, the transfer of ions from a solution containing enough supporting electrolyte to the electrode surface is realized by spherical diffusion which is considerably more rapid than in ordinary polarography. As a result the concentration gradient in the layer near the electrodes is greater than the value of $(dc/dr)_{r=0}$ in the effective diffusion layer obtained as the result of a slow increase in applied potential, i.e. as in the case of ordinary polarography. Thus for an equal concentration of the test ion the value of the maximum current of the reduced ion is considerably greater than the value of the limiting current. On applying a saw-tooth potential to the cell the diffusion rate varies with the time, as can be seen from the oscilograms shown in Figs. 9 and 10.

The electrochemical reaction itself proceeds very rapidly and the slow stage of the process is the diffusion stage. As a result the overall velocity of the electrochemical transformation is determined by the rate of spherical diffusion to the stationary mercury surface which is the slowest stage of the process. In the case of the saw-tooth method however the removal of reaction products from the mercury drop surface is of essential significance. This stage of the process is slow in comparison with the rate at which the saw-tooth voltage is applied, and also shows an effect on the value of the maximum current of the reduced ion. Since under saw-tooth operating conditions the next increase in potential follows on immediately after the sudden drop of the previous impulse, i. e. when the ions reduced on the dropping electrode have not yet succeeded in being completely oxidized and distributed in the layers which are further removed from the electrode surface, then some of the oxidized ions remain near the electrode, as a result of which the concentration gradient in the diffusion layer becomes less than that forecast if only symmetrical spherical diffusion to the stationary electrode for a rapid potential change on the electrode is taken into account. In practice, as a result, the values of the current obtained are low in comparison with the true values of the polarographic current calculated from the diffusion equation.

What has been said is illustrated by the curves adduced in Fig. 18. Concentration of cadmium in mols/liter is plotted along the abscissa while the maximum current for Cd^{2+} is plotted along the ordinate. From the results given in Fig. 18 it follows that in the case of the impulse method the values of I_{max} are considerably greater than those obtained by the saw-tooth method.

Experiments, the results of which are given in Table 1 show that the significant deviation of experimental results from the calculated values is probably a result of the fact that Randles and Seveik in deriving their respective equations for the maximum current used the differential equation for linear diffusion instead of the equation for spherical diffusion, and of the fact that they did not take into account the rate of removal of the reaction products from the surface of the mercury drops when using the saw-tooth method. It follows from the results given in Table 1 that with increasing rate of saw-tooth potential change the maximum current of the reduced ion increases.

On a mercury electrode with a low drop rate the values of the maximum current of the reduced ion are considerably greater than I_{max} obtained on an electrode with short drop time. Compare in Table 1 experiments carried out for practically the same values of $\alpha^{1/2}$, e. g. for 3.006 and 3.077 and for 3.536 and 3.544. The reverse is observed in ordinary polarography. For a slow dropping electrode the values of the limiting current are less than I_{max} obtained when using a capillary with a short dropping period. E. g. for $5.9 \cdot 10^{-3}$ M $CdCl_2$ in 0.1 M KCl using a capillary for which m = 4.6 mg/sec and t = 2.36 sec, it was found that the limiting current is equal to 35.34 μA while in a solution of 0.1 M KCl containing $6.5 \cdot 10^{-3}$ M $CdCl_2$ using a capillary with the characteristics; m = 0.847 g/sec and t = 7.33 sec, $I_{limiting}$ was 28.21 μA.

By solving the equation for non-stationary diffusion to a stationary spherical mercury electrode and taking into account the concentration distribution of reaction products at various distances from the surface of the mercury drop when operating under saw-tooth voltage conditions, we got the following semi-empirical equation for the maximum current of the oscillographic wave:

$$I_{max} = 1034.4n^{3/2}cD^{1/2}m^{2/3}t^{2/3}\alpha^{1/2} - 8425n^3c^2Dm^{4/3} \qquad (7)$$

where m is expressed in mg/sec; c is the concentration in millimols/liter.

TABLE 2

Effect of Rate of Potential Change on the Value of the Maximum Current of Cadmium.

$1.039 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10^{-5}$ cm²/sec.; m = 0.835 mg/sec.; t_{max} = 8.44 sec.; h = 270 mm; experimental temperature 25.0° ± 0.1°

$\alpha^{1/2}$ where α is the rate of potential change in V/sec.	Maximum current of the reduced ion		Difference in % between calculated and experimental results
	Found in μA	Calculated by means of equation (7) in μA	
1.686	3.97	4.15	−4.37
2.016	4.79	4.93	−2.73
2.363	5.73	5.74	−0.16
2.509	5.95	6.07	−1.98
2.795	6.5	6.72	−3.23
3.006	7.50	7.20	+4.16
3.536	8.38	8.37	+0.09

The remaining legends are the same as in equations (2) and (4). The maximum current is expressed in microamperes.

Using equation (17) we calculated the maximum current for cadmium and compared the results obtained with experimental results. Both calculated and experimental results are given in Table 2. Calculated values are taken as 100%.

Table 2 shows that experimental and theoretical results are in good agreement.

The respective equations of Randles and Seveik were derived for reversible electrode processes. For irreversible processes, Delahay [19], proposed the following equation for the maximum current of the oscillographic wave.

$$I_{max} = 2.56 \cdot 10^5 n(an_a)^{1/2}m^{2/3}t^{2/3}D^{1/2}c\alpha^{1/2} \text{ amperes} \qquad (8)$$

where a is a coefficient characteristic of the degree of irreversibility of the electrode process; n_a − the number of electrons participating in the reaction which determines the reaction velocity; c − the concentration in mols/cm³; m − the amount of mercury in g issuing from the capillary/sec. The remaining legends are the same as in equations (2) and (4).

Equation (8) has not been checked experimentally.

B. The Capacity Current on Oscillographic Curves

The existence of a current independent of whether or not electrode processes occur on the electrode surface is related to drop growth and to the presence of a double electrical layer on the boundary between drop and solution. Drop growth at a constant potential, independently of any electrochemical reactions, is accompanied by a current which is called the charging current. When the applied

voltage is less than 0.5 V relative to the normal calomel electrode, the current which passes is negative, i. e. it is in the reverse direction to that of the reduction current. At higher potentials it changes its sign.

In oscillographic polarography, as the result of a rapid increase in the potential applied to the cell and the shape of the impulse applied to the dropping electrode, the capacitor current is considerably greater than the charging current obtained in ordinary polarography.

When a saw-tooth voltage is applied to the cell, it is reckoned [20] and [21], that the capacitor current may be expressed by the following equation:

$$i_c = 0.00846\ m^{2/3}t^{2/3}c\,dE/dt \text{ microamperes} \qquad (9)$$

where m – is the amount of mercury issuing from the capillary/sec; c – the capacity of the double layer in micro-farads $(\mu F)/cm^2$, t – the dropping time of the capillary, dE/dt – the rate of change of potential.

Delahay and Stiehl [22], suggested the formula given below, which differs somewhat from equation (9):

$$i_c = 4.81(m/d)^{2/3}t^{2/3}\left[E\frac{dc}{dE} + c\right]\frac{dE}{dt} + 3.20c(m/d)^{2/3}t^{-1/3}E, \qquad (10)$$

where E – is the value of the saw-tooth voltage applied to the cell; and d – the density of mercury. The other legends are the same as in equation (9).

The capacitor current must be considered at a definite value of the maximum current. Distortion of the oscillographic wave can be considerable when I_{max} is less than the charging current. Usually the value of the maximum current is determined graphically as shown in Fig. 19. In curve A the charging current initially increases rapidly and becomes constant at the reduction or oxidation potential of the ion. By producing the line for the capacitor current paralled to the abscissa the value of the maximum current can be determined.

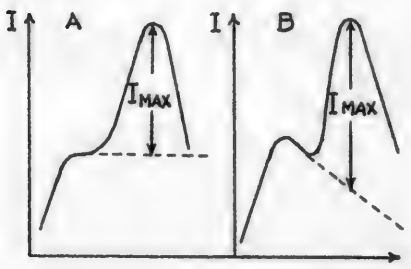

Fig. 19. Measuring the value of the maximum current without taking into account the capacitor current.

When the oscillographic curve has the shape shown in Fig. 19 B, the line is produced as shown in Fig. 19 and I_{max} calculated. When concentrations of less that 10^{-3} mol/liter are dealt with, it is necessary to establish by means of a separate experiment the capacitor current from an oscillogram for a solution of the supporting electrolyte at the same potential at which the maximum current is measured. The value of the charging current thus obtained is subtracted from the value of I_{max}.

III. Qualitative Analysis.

Heyrovsky [11,23], was one of the first to use an oscillographic method for qualitative analysis. The voltage-time curves and their derivatives obtained by means of an oscillographic polarograph (Fig. 17) permit one to detect various ions in solution from their half-wave potentials or from their oscillographic spectra. If one or more steps are formed on the voltage-time curve, then by using a high frequency generator it is possible to draw out the steps so that they assume the form of spectral lines. Fig. 20 illus-

trates the spectral lines obtained for a solution of 0.5 N NH_4OH + NH_4Cl containing $HgSO_3^{2-}$, Tl^+, Cd^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}. The positions of these lines on the ordinate scale, i. e., their potentials, correspond to the usual half-wave potentials obtained when using ordinary polarography. By comparing this empirical scale of deposition potentials with the potentials of the edge lines of the spectra, which depend on the composition of the supporting electrolyte, it is possible to carry out qualitative determinations.

If there are no means available for registering the spectra, then it is still possible to carry out qualitative determinations by establishing the positions of peaks on the voltage-time curve. In this way it is possible to detect inorganic and organic depolarizers in concentrations from 10^{-4}N.

Heyrovsky [24], also developed a method of getting dE/dt – E curves. Such curves in certain instances give more information than an ordinary polarogram, since the effect of anode polarization which does not appear on current-voltage curves, i. e., in ordinary polarography, can in addition identify the depolarizer [11]. Indium which cannot be determined polarographically in the presence of cadmium is recorded on the anode branch of the dE/dT – E curve, as can be seen from the diagram adduced in Fig. 20 B. This diagram was recorded for a zinc ore containing traces of lead, cadmium, and indium. The dE/dt – E curves are particularly valuable for the analysis of mixtures of organic isomers. In such a case when a dropping mercury electrode is used, very complex curves are obtained because of side reactions. On the other hand, a streaming electrode [25] is polarized to give a simple picture with minima at characteristic potentials whereby it is possible to distinguish [26, 27] ortho-, meta-, and para-nitrophenols in the presence of nitrobenzene. Similarly the isomers: nicotinic, picolinic, and isonicotinic acids can be distinguished in 2 N sulfuric acid.

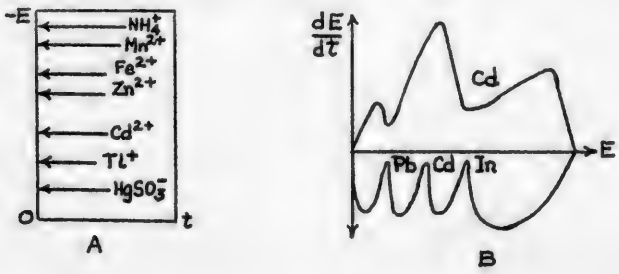

Fig. 20 A – Scale of the spectrum in 0.5 N NH_4OH + NH_4Cl; B – the curve dE/dt – E for 2 N sodium hydroxide – potassium cyanide. Upper curve, cathode process; lower curve, anode process.

Atmospheric oxygen only affects derivative curves in acid media and even here does not interfere with this type of analysis too much.

When a dropping electrode is used for oscillographic studies it is sufficient to use only a few mls of solution in a small, open beaker.

When a streaming electrode is used, 15 – 18 ml of solution is required. Qualitative measurements of half-wave potentials obtained by oscillographic methods by Miller [28], and Boeke and Suchtelen [29], are comparable in accuracy with ordinary polarography. E.g., Miller got a half-wave potential for cadmium of −0.627 - 0.629 V relative to the saturated calomel electrode, which is in good agreement with the result of ordinary polarography.

Snowden and Page [8] differentiated the I – E curve to get "breaks" on the oscillographic curve at points near to the maximum current. The potentials at which these breaks were obtained gave an indication of the qualitative composition of the test solution.

The GEOKhI oscillographic polarograph [7], which operates on a saw-tooth voltage permits evaluation of the qualitative composition of a solution from the potentials corresponding to peaks on the I – E curves.

IV. Quantitative Analysis.

According to equations (5), (6), (7), and (8) the values of the maximum diffusion current are proportional to the concentration of test material in solution when saw-tooth or impulse methods are employed. It has been shown experimentally [4,5,7,10], that the linear relation between I_{max} and concentration of test material in solution both for reversible and irreversible processes only holds for a constant rate of potential change and for equal pressures on the dropping mercury.

As illustrations, we have adduced in Tables 3, 4, and 5 results obtained using the GEOKhI polarograph in the absence of atmospheric oxygen.

TABLE 3

Maximum value of the current for various concentrations of cadmium in 0.1 N KCl;

h = 270 mm; m = 0.347 mg/sec.; t = 14.5 sec.; α = 17.27 V/sec.

Concentration of cadmium, in mol/liter	Maximum value of current, in μA
$1.039 \cdot 10^{-4}$	12.57
$5.195 \cdot 10^{-5}$	6.32
$1.039 \cdot 10^{-5}$	1.28
$5.195 \cdot 10^{-6}$	0.68
$1.039 \cdot 10^{-6}$	0.14
$5.195 \cdot 10^{-7}$	0.08

TABLE 4

Maximum values of the current for various concentrations of lead in the presence of copper and zinc in 0.1 N KNO_3

m = 0.352 mg/sec.; t = 11.3 sec; α = 11.16 V/sec.

Concentration of lead, in μg/ml	Maximum value of the current, in μA
20.8	6.93
10.4	3.42
5.2	1.70
2.08	0.81
1.04	0.43
	–

The results in Table 3 show that there is a linear relation between maximum current and cadmium ion concentration; there is a slight deviation from linearity when dealing with very dilute solutions.

The sensitivity of the oscillographic method is considerably higher than that of ordinary polarography, the latter can only determine 10^{-5} M $CdCl_2$ when a multi-capillary mercury electrode is used [30]. At concentrations less than 10^{-5} mol/liter we could not get a definite cadmium wave on the voltage-ampere curve obtained with an ordinary Heyrovsky polarograph because it fused into the supplementary current wave [37].

The results given in Table 4 show that the linear relation between lead concentration and the maximum current for lead is maintained in the presence of accompanying ions. Two oscillograms are given in Fig. 21 for potassium nitrate containing copper, lead, and zinc. E = –0.9 V was chosen in this case for lead determination. The oscillograms were recorded for one drop of mercury at its maximum cross-section corresponding to the moment at which the drop is about to fall off, at a rate of potential change of 9.8 V/sec.. The oscillograms, which are really voltage-ampere curves, show from the left a sharp rise on the curve caused by the discharge current of the mercury sur-

face and the shape of the applied impulse and by the reduction of the copper. This is followed by a sudden drop until lead is reduced on the dropping mercury cathode; this occurs at an amplitude value of the saw-tooth voltage of − 0.8 V relative to the anode mercury. The lead waves are clearly defined and can be measured exactly.

The lead waves on Curves 1 and 2 correspond respectively to 20 and 10 μg/ml. The values of the maximum current of lead are respectively 5.23 and 2.62 μA, which indicate a strict linearity between concentration and $I_{max.}$.

Cadmium and lead ions are reduced reversibly on the dropping mercury electrode, while Zn^{2+} is irreversibly reduced (re reversible and irreversible processes, see below).

In order to check whether or not there is a linear relation between the concentration of the reduced ions and the value of its maximum current for irreversible processes, a number of experiments were carried out on the electrolysis of Zn^{2+} solution.

Table 5 contains results of the maximum current of zinc in 0.1 N KNO_3 in the presence of lead and copper ions.

TABLE 5

Maximum values of the current for various concentrations of zinc in the presence of lead and copper in 0.1 N KNO_3; m = 0.347 mg/sec.; t = 12.5 sec.; α = 18.6 V/sec.

Zinc concentration in μg/ml	Maximum values of the current in μA
9.90	11.91
4.90	6.03
1.88	2.41
0.94	1.24
0.47	0.64

These results show that a linear relation exists between concentration of zinc ions in solution and the maximum current of zinc. At very high dilutions there is some deviation from linearity. Experiments on zinc determinations showed that the sensitivity of the oscillographic method can be increased up to 10^{-6}%.

By means of the oscillographic polarograph it is possible to determine titanium quantitatively in the presence of considerable amounts of iron and vanadium without preliminary separation of the latter; this is however impossible to carry out by ordinary polarography in which the Fe (III) and V (V) have to be separated beforehand from the titanium [31].

What has been said is illustrated by the curve adduced in Fig 21. These curves were obtained in 1 N H_2SO_4 saturated with sodium oxalate; 1 ml of the respective solutions contained:

10 μg Ti(IV) + 40 μg Fe(III); 10 μg Ti(IV) + 40 μg V(V);
10 μg Ti(IV) + 75 μg V(V) + 500 μg Fe(III).

The first and second curves were obtained with an ordinary polarograph. For an iron content 4 times greater than that of titanium the polarogram of the latter is distorted and a maximum is obtained on the E − I curve (Curve 1, Fig. 22).

When the concentration of vanadium is four times that of titanium, a maxi-

mum appears on the curve and the limiting current decreases with increasing applied potential. The origin of the curve is not clearly defined either (Curve 2, Fig. 22). Curve 3 represents an oscillographic photograph of the process occurring on a mercury drop of maximum size. A titanium wave is clearly defined on the E – I curve, this appears at an amplitude of the saw-tooth voltage of –0.30 V relative to the saturated calomel electrode.

It was established that if the amount of iron and vanadium were 100 and 20 times respectively that of Ti (IV), then they have practically no effect on the value of I_{max} for titanium. On a basis of the study of the effect of accompanying elements we succeeded in working out a rapid method for the determination of titanium in steels without preliminary separation of vanadium and iron [31].

V. A Study of the Reversibility of Electrode Reactions.

Any electro-chemical reaction can be considered either as reducing, when the reactants acquire electrons (on the cathode) or as oxidizing when they donate electrons (to the anode). Oxidation-reduction reactions are usually divided into reversible and irreversible reactions.

A reversible reaction is one which satisfies the following conditions:

a) When an inert electrode is immersed in the test solution a definite potential is established on the electrode, which depends only on the concentration and nature of the oxidized and reduced reaction products. Its potential should be independent of the material and the state of the surface of the electrode.

b) On passing a current of sufficiently low density through the electrode its potential should be hardly displaced at all from its equilibrium value, and should not take into account concentration polarization.

Oxidation-reduction reactions which do not satisfy these conditions are called irreversible. Each time there is an electrochemical reaction with a measurable velocity, i. e., every time current passes through the electrode, this leads to some break-down in the thermodynamic equilibrium, and thus leads to a shift in the electrode potential from its equilibrium value.

In the case of the dropping mercury electrode the half-wave potential ($E^{1/2}$) of a simple metal ion depends on the equilibrium potential of the metal, its solubility in mercury and its affinity for mercury [32]. Theoretical values of $E^{1/2}$ have been worked out for some ions and have been compared with experimental values [33]. It was found that the half-wave potentials of lead and zinc do not differ appreciably from the ordinary normal potentials of these metals; this indicates the reversibility of these electrode processes.

Oscillographic polarography has shown however that Zn^{2+} is reduced irreversibly on the dropping mercury electrode, since the cathode and anode processes occur at different potentials. This example shows that it is better to study reversibility and irreversibility of electrode processes by means of oscillographic polarography than by ordinary polarography (from the value of the slope of the straight line obtained by graphical analysis of the equation for the polarographic wave) [33].

In polarography a reversible electrode process is that process for which both cathode and anode processes occur at the same potential while the rates of the two processes are so fast that the current is determined only by diffusion.

Heyrovsky [11, 34], used the term " oscillographic irreversibility" for emphasizing the differences between anode and cathode processes. At present some authors prefer to consider the question of irreversibility from three view-points.

1) Anode and cathode processes occur rapidly enough at various half-wave potentials. This implies a different mechanism for the two processes.

2) Anode and cathode processes occur at the same potentials, but the rates of the reduction or the oxidation processes, or of the two together, are low, diffusion is not of great significance, and the limiting current is determined only by the kinetics of the electrode reaction.

3) The third view point is a combination of both the other two. The first two are the view-points most often met in the literature.

The irreversibility of an electrode process in oscillographic polarography is manifested on the curves in various forms. E.g., if a saw-tooth voltage is applied to the cell and the process is irreversible then the peak on the oscillographic curve I - E will be more obtuse than if the process is reversible. If an irreversible process is observed during electrolysis, then on using a triangular sweep, $E^{1}/_{2}$ will not coincide on the cathode and anode branches of the I - E curve. From the extent of the deviation of the half-wave potentials of the oxidation and reduction processes it is possible to judge the degree of irreversibility [10] (see Fig.15). If the electrode process is reversible then on the potential - time curves obtained by means of a Heyrovsky oscillographic polarograph, a symmetrical arrangement of steps will be obtained on the ascending and descending branches of the curve (see Fig.17). When this technique is used and an irreversible process occurs on the electrode, steps are again observed on the cathode and anode branches of the curve but not at the same potential. The degree of irreversibility of an electrode process can also be established from the deviation of the value of the maximum current (on the I - E curve) from the value of I_{max}, calculated by means of equation (7), for various values of potential change (see Table 2). Finally, it is possible to determine the degree of irreversibility of an electrode process from the relation between maximum current and mercury pressure. For reversible systems, the maximum current is, theoretically, independent of mercury pressure [see equations (5), (6), and (7)].

1. I - E Curves.

a). The shape of the peak on the I - E Curve. Randles [14] investigated the reduction of several ions on a dropping mercury electrode in order to study the reversibility and irreversibility of electrode processes; he established that reversible reactions under saw-tooth operating conditions are characterized by an acute peak, as in the case of the reduction of Cd^{2+} in 1 N KCl (Fig.23, A). For reactions which deviate from reversibility more obtuse peaks are obtained on the I - E curve, as in the reduction of zinc in 1 N KCl (Fig.23, B). Nickel and cobalt give even more obtuse peaks on the I - E curve than Zn^{2+}, since the degree of irreversibility is more marked in Ni^{2+} and Co^{2+} than in Zn^{2+}. The shape of the peak also depends on the number of electrons participating in the electronic reactions. For Bi^{3+} the peak is more acute than for Cd^{2+}, while the latter has a more acute peak than thallium.

b). The Value of the Maximum Current. According to equations (5), (6), and (7), the value of the maximum current should depend on the rate of change of saw-tooth potential applied to the cell (α).

Delahay [16], studied the effect of $\alpha^{1/2}$ on the value of the maximum current of the reduced ion and compared the experimental results with values calculated by means of Randles' and Seveik's equations. He got an insignificant deviation between the values of I_{max} for Tl^{+} calculated by Randles' equation and the experimental values. For Pb^{2+} and Cd^{2+}

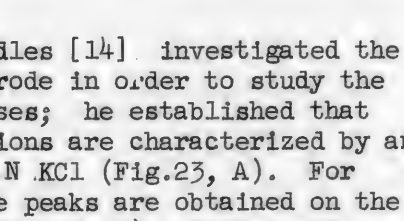

Fig. 23. Shape of the oscillographic curves for saw-tooth sweeps.
A - for the reduction of Cd^{2+} in 1 N KCl; B - for the reduction of Zn^{2+} in 1 N KCl.

however, the deviations were considerable. Significantly greater deviations between the theoretical and experimental values of the maximum current were found for Ni^{2+} and the iodate ion, which are reduced irreversibly on the dropping mercury electrode. These considerable deviations between theory and experiment cannot, however, be attributed entirely to the characteristics of the electrode reactions, since cadmium and lead are reduced reversibly on the mercury electrode. These deviations are predominantly caused by the mechanism of electrolysis during the rapid increase of the saw-tooth voltage on the cell [35,36]. Since equations (5) and (6) do not take into account the characteristics of electrolysis during saw-tooth voltage operating conditions, they cannot serve as criteria for explaining the degree of irreversibility of an electrode process (ee the results given in Table 1).

The electrolysis conditions which hold for saw-tooth operating conditions were taken into account in deriving equation (7), so that it is possible to use the equations for studying the degree of irreversibility of an electrode process (see the results given in Table 2).

According to equations (5) and (6) the value of the maximum current is proportional to the product $m^{2/3} \cdot t^{2/3}$, i.e. to the drop surface. Since the latter is independent of the pressure of the mercury column, it can be deduced that, if all the other factors included in equations (5) and (6) are constant, then I_{max} does not depend on the height of the mercury column [6]. As examples we have adduced a number of curves in Fig.24 which relate maximum current to the height of the mercury column. The height of the mercury column is plotted along the abscissa, while the percentage deviation from the value of the maximum current obtained for a mercury column of height 15 cm is plotted along the ordinate (the value of I_{max} at a mercury column height of 15 cm is arbitrarily taken as 100%).

Fig.24 shows that the value of the maximum current does depend to some extent on the height of the mercury column. Insignificant deviations from a straight line are observed for Cd^{2+}, and Pb^{2+}; greater deviations are obtained for Zn^{2+} because Zn is irreversibly reduced on the dropping mercury electrode.

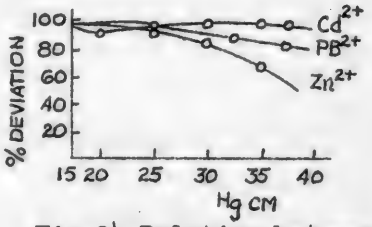

Fig.24. Relation between maximum current and height of mercury column.

c) I - E Curves obtained by means of Triangular Voltage Impulses.

I - E curves obtained by means of Seveik's set-up [10] have the advantage of giving a complete picture of the electrode process, showing cathode and anode processes. A typical I - E curve is shown in Fig.15. Seveik [10] points out that in order to find the half-wave potential on the cathode branch of the curve it is necessary to add $40/n$ mV[1] to the value found for the potential at which the current has its maximum value, where n is the number of electrons participating in the electrode reaction. To determine $E_{1/2}$ on the anode branch of the curve, the same factor has to be subtracted from the value of the potential at which I_{max} is obtained. If the potentials of the two half-waves are the same, then the electrode process can be regarded as reversible. An I - E curve obtained for a reversible process is shown in Fig.15

During the electrolysis of a solution of 1 N NH_4Cl and 1 N NH_4OH, containing zinc, Seveik found that the value of $E_{1/2}$ on the cathode branch differed from that on the anode branch by 0.22 V. This difference between the two half-wave potentials on the respective curves shows that in ammoniacal solutions zinc is reduced irreversibly. The I - E curve obtained for zinc in ammoniacal solution is shown in Fig. 25 A. If to 1 N HCl containing Cd^{2+} there is added freshly prepared gelatin solutions, so that its concentration is 0.005%, then the I - E

1) See Seveik's articles [10], Equations 1, 24.

curves shown in Fig. 25 B which are of a different shape are obtained. No peaks are obtained on the cathode and anode branches of the curve. A small increase in current is observed on both branches of the I - E curve. Fig.25 B shows that even insignificant amounts of freshly prepared gelatin added to the test solution leads to a hindering of the electrochemical processes.

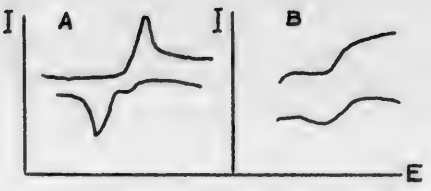

Fig.25. Voltage-current curve (I - E) for irreversible processes.

A - Zn^{2+} in ammoniacal media; B-ditto as in A but with gelatin added.

2. E - t Curves Obtained by Means of A Heyrovsky Oscillographic Polarograph.

Heyrovsky studied the reversibility and irreversibility of electrode reactions by means of voltage-time curves [11, 23, 25, 34, 37, 38]. If a reaction is rapid enough and is reversible as in the reduction of cadmium, lead, and thallium ions in 1 N KCl or in HNO_3, then the cathode and anode steps are found to occur at the same potential; as a result a symmetrical curve of the type shown in Fig. 26 A is obtained. The dotted line represents the E - t curve obtained before addition of the depolarizer. The width of the step is a function of depolarizer concentration. When the reaction is irreversible an unsymmetrical E - t curve is obtained in which the step occurs at a more positive potential on the anode branch of the curve than on the cathode branch. The reduction of Zn^{2+} on a dropping mercury cathode in KCl, NH_4OH, or KOH (Fig. 26 B) is an example of an irreversible electrode reaction.

TABLE 6

Reversible Reactions

Element	Supporting Electrolyte	Electrode reaction
Cu^{2+}	1 N NH_4OH + 1 N NH_4Cl	$Cu^{2+} + e \rightleftharpoons Cu^{+}$
Cu^{+}	1 N NH_4OH + 1 N NH_4Cl, 1 N KCl	$Cu^{+} + e \rightleftharpoons Cu$
Sb^{3+}	1.0 N HCl	$Sb^{3+} + 3e \rightleftharpoons Sb$
Bi^{3+}	1.0 N HCl	$Bi^{3+} + 3e \rightleftharpoons Bi$
Sn^{2+}	2 N $HClO_4$ + 0.5 N HCl	$Sn^{2+} + 2e \rightleftharpoons Sn$
Pb^{2+}	1.0 N KCl; 1.0 N NaOH; 1 N KCN	$Pb^{2+} + 2e \rightleftharpoons Pb$
U^{6+}	1 N KCl	$U^{6+} + e \rightleftharpoons U^{5+}$
Tl^{+}	1 N KCl; 1 N HCl; 1 N NaOH	$Tl^{+} + e \rightleftharpoons Tl$
In^{3+}	0.1 N KCl; 1 N KCl	$In^{3+} + 3e \rightleftharpoons In$
Cd^{2+}	1 N KCl; 1 N HCl; 0.1 N KCl; 0.1 N HCl	$Cd^{2+} + 2e \rightleftharpoons Cd$
Cr^{3+}	0.1 N KCl	$Cr^{3+} + e \rightleftharpoons Cr^{2+}$
Fe^{3+}	0.1 N KCl	$Fe^{3+} + e \rightleftharpoons Fe^{2+}$
Ni^{2+}	1 N KCN	$Ni^{2+} + 2e \rightleftharpoons Ni$
Co^{2+}	1 N KCN	$Co^{2+} + 2e \rightleftharpoons Co$
Mn^{2+}	0.5 — 1 N KCN	$Mn^{2+} + e \rightleftharpoons Mn^{+}$
Na^{2+}	0.1 N $N(CH_3)_4Cl$ or 0.1 N $N(CH_3)_4OH$	$Na^{+} + e \rightleftharpoons Na$
K^{+}	0.1 N $N(CH_3)_4Cl$ or 0.1 N $N(CH_3)_4OH$	$K^{+} + e \rightleftharpoons K$

TABLE 7

Irreversible Reactions

Element	Supporting electrolyte	Electrode reaction	Difference in value between $E_{1/2}$ on cathode and anode branches of curve	Slow electrode process
Cu^{2+}	0.1 N Na_2SO_4; 0.1 N KNO_3	$Cu^{2+} + 2e = Cu$	Observed	-
Bi^{3+}	0.3 M tartrate or citrate pH 4.5	$Bi^{3+} + 3e = Bi$	Observed	-
In^{3+}	0.1 N $HClO_4$	$In^{3+} + 3e = In$	Observed	-
Cd^{2+}	1 N KCN	$Cd^{2+} + 2e = Cd$	-	+
Sn^{2+}	1 N H_2SO_4	$Sn^{2+} + 2e = Sn$	-	+
Co^{2+}	1 N KCN	$Co^{2+} + 2e = Co$	-	+
Co^{2+}	0.1 N KCl	$Co^{2+} + 2e = Co$	-	anode
Zn^{2+}	1 N NH_4OH + 1 N NH_4Cl	$Zn^{2+} + 2e = Zn$	Observed	-
Ni^{2+}	0.1 N KCN	$Ni^{2+} + 2e = Ni$	-	+
Ni^{2+}	$(CH_3)_4NBr, CN^-, Cl^-$	$Ni^{2+} + 2e = Ni$	-	anode
Mn^{2+}	1 N KCl; 1 M NH_4OH+1 M NH_4Cl	$Mn^{2+} + 2e = Mn$	Observed	anode
Fe^{2+}	0.1 N KCl	$Fe^{2+} + 2e = Fe$	Observed	anode
Cr^{2+}	0.1 N KCl	$Cr^{2+} + 2e = Cr$	Observed	-
Al^{3+}	0.1 N LiCl	$Al^{3+} + 3e = Al$	-	anode
In^{3+}	0.1 N HCl	$In^{3+} + 3e = In$	-	cathode
Eu^{3+}	no supporting electrolyte	$Eu^{3+} + e = Eu^{2+}$	-	+
Ti^{4+}	0.1 N HCl	$Ti^{4+} + e = Ti^{3+}$	-	+
IO^{3-}	0.1 N KOH 0.1 N H_2SO_4	$IO^{3-} + 6e = I^-$	-	+
CH_3NO_2	acetate buffer	$-NO_2 + 4e = =-NHOH$	-	no anode wave
$C_6H_5NO_2$	acetate buffer	$-NO_2 + 4e = =-NHOH$	-	no anode wave

By means of E – t curves Heyrovsky studied reduction mechanisms for thallium, lead, cadmium, tin, bismuth, antimony, indium, chromium, manganese, iron, cobalt, nickel, and copper on a dropping mercury cathode. The reversibility of the reactions of many organic materials was also studied. E.g., Heyrovksy showed that maleic acid is reduced irreversibly on the dropping mercury cathode. Heyrovsky also used a streaming mercury electrode [25], for studying reversibility and irreversibility of electrode processes.

Using the results of a study of the reversibility and irreversibility of certain electrode processes we have listed in Table 6 those reactions which were found to be reversible by an oscillographic method. Table 7 contains a list of those reactions which were found to be irreversible according to the oscillographic method. The speed with which the reaction proceeds on the surface of the mercury electrode is of essential importance in the case of irreversible electrode reactions. A decision as to whether or not a reaction is slow or fast can be made from a comparison of the rates of the two reactions. When the reaction velocity of the same electrically

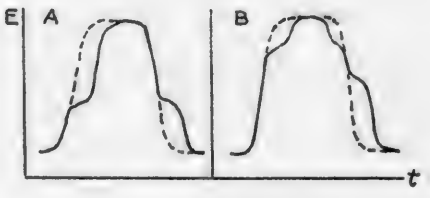

Fig.26 Voltage - time (E - t) curves.
A - for a reversible reaction;
B - for an irreversible reaction

reduced material in different supporting electrolytes varies, e.g. the rate at which nickel is reduced in a solution of KCN is greater than the rate at which it is reduced in KCl, then the first reaction can be regarded as fast and the second, slow.

When the reaction velocity of the two different electrically reduced materials in the same supporting electrolyte differ considerably from each other, e.g. cadmium in KCl is reduced considerably more rapidly than cobalt in KCl, then the cadmium reaction can be regarded as fast and the cobalt reaction as slow.

Table 7 includes two additional columns; one of them contains information as to whether or not there is a difference in the potentials on the cathode and anode branches of the curve; and in the other information as to which reaction is the slower. If both reactions are slow (anode and cathode) then a plus sign is given in this column. If one is slower than the other, then information is given as to which reaction is the slower.

SUMMARY

1. Original designs of oscillographic polarographs by means of which various oscillographic curves can be obtained are discussed: I - E, E - t, dE/dt - t.

2. The respective equations of Randles and Seveik for the maximum current are considered. It has been shown that the experimental results do not agree with the values of the maximum current calculated by means of Randles' and Seveik's equations, respectively, when using saw-tooth voltage conditions. Seveik's equation can be corrected when operating under impluse conditions.

3. A new equation is suggested for the maximum current; this equation only holds for saw-tooth voltage operating conditions.

4. It has been shown that it is possible to establish the qualitative composition of a solution and to carry out quantitative determinations of inorganic and organic compounds by means of oscillographic polarography.

5. It has been shown that it is better to study the reversibility and irreversibility of electrode reactions by means of oscillographic polarography rather than by ordinary polarography.

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A FLAME PHOTOELECTRIC METHOD FOR THE DETERMINATION OF CALCIUM IN SOLUTION

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The acetylene-air flame excites radiation from only a limited number of elements. The spectrum consists of a few lines, the wave-lengths of which differ considerably from each other. This fact permits a comparatively easy separation of the characteristic radiation of some elements by means of light filters. The intensity of the radiation isolated can be measured photoelectrically and is a function of the concentration of the element fed into the flame. The fact that the burning conditions of the flame are steady, and the steady rate at which test material can be fed into the flame as a solution, permit one to carry out analysis by means of the absolute intensity of the radiation.

The author has previously described [1], a quantitative method for the determination of sodium and potassium in soils in which light filters are used as follows. Using an atomizer and a burner (Fig. 1) the test solution is fed into the flame. The radiation of sodium 5890/95 A and potassium 7665/99 A are isolated with filters with maximum transmission at the wave length of the radiation being measured.

The isolated sodium radiation falls on a selenium photo-element while that of the potassium falls on a sulfide-silver element. The photo-current is measured with a mirror galvanometer with a sensitivity of $10^{-9} - 10^{-10}$ A. The concentration of test element can be measured from 1 mg/liter or $1 \cdot 10^{-4}$% upwards of test solution by means of calibration curves.

It has been shown that the presence of aluminum, iron, and magnesium in the test solution in amounts of 0.1% have practically no effect on sodium and potassium determinations. Neither does potassium interfere with sodium determinations and vice-versa. The presence of calcium in solution however does lead to high results for sodium and to a lesser extent for potassium. This interference on the part of calcium has been noted by a few authors [2, 3, 4, 5], who recommend removal of calcium from solution or application of suitable corrections.

The high values obtained for sodium and potassium are the result of the rather wide and intense bands of calcium with maxima at 5500 A and 6150 A, and insufficiently complete separation by the light filters. The filter not only transmits the radiation of the test elements but also that of the bands and background of calcium so that the photo-current measured is a sum of various photo-currents.

This fact necessitates taking this additional photo-current of calcium into account, and compensating for it as follows.

A filter with maximum transmission at 6200 A is used to isolate the calcium radiation at the bands noted above. The isolated radiation is directed on to a selenium photo-element which is connected in a direction reversed to that of the

photoelements designed for sodium and potassium determinations (Fig. 2). It is thus possible to compensate the photocurrent caused by calcium when the filters used for sodium and potassium determinations are not sufficiently monochromatic, by opposing to this current another one from an isolated calcium band. In practice this is achieved as follows.

A solution of calcium free from sodium and potassium is fed into a flame. By adjusting a diaphragm on the compensator filter a galvanometer reading is obtained at which there is no change whether calcium is fed into the flame or not. This position is the "null" point; it is not changed during an analysis. The calcium content should be roughly the same as in the test solution.

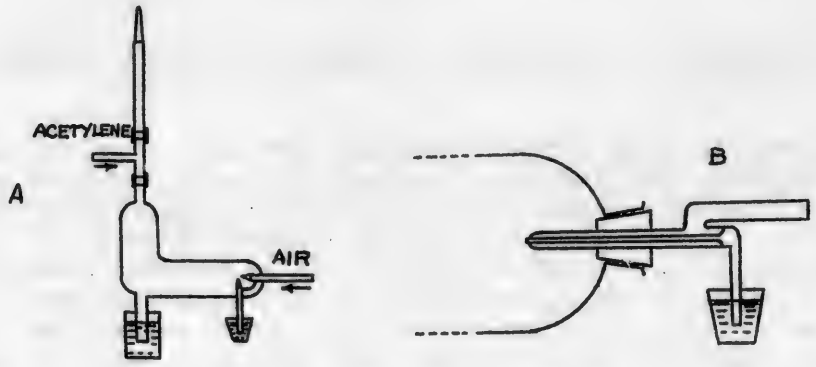

Fig. 1 A) Atomizer and burner; B) part of the atomizer with an injector of another type.

The Ca-filter is not completely monochromatic either, and does transmit Na and K radiations to some extent. By compensating through using the diaphragm it is possible to get conditions under which practically no Na and K radiation is transmitted. This is also true of the Na-filter and the K-filter when it is necessary to compensate for Na and K during Ca determinations.

Tests showed that the calibration curves for sodium and potassium constructed by means of the pure solutions or with solution containing calcium (500 mg/liter) coincide entirely, starting from concentrations of 1 mg/liter of the test element. The accuracy of sodium and potassium determinations in the concentration range 1–100 mg/liter is ca. $\pm$ 5%.

The general appearance of the set-up is shown in Fig. 3.

It is natural that the question of determining calcium on the same set-up arises. Calcium gives a very strong line at 4227 A in the flame, and two bands with maxima in the regions 5500 and 6150 A. The absence of suitable photoelements means that the fundamental line cannot be used, while a comparison of the bands showed that by using the latter band a considerably higher sensitivity can be achieved.

In order to isolate the red calcium band a light filter with maximum transmission at 6200 A was used; the isolated radiation was directed on to a selenium photoelement. The photo-current was measured using a mirror galvanometer with a sensitivity of $10^{-9} - 10^{-10}$ A.

Accurate quantitative determinations of solutions containing 5 mg/liter were shown to be possible. The calibration curve is a straight line up to concentrations of calcium of 4000 mg/liter. Further study showed that quantitative determination of calcium in solution is accompanied by difficulties which are closely related to the intensity of the calcium radiation when other cations and

anions are present in solution. These difficulties are either usually not met with at all or present little trouble in determinations of sodium and potassium.

In our tests we found that calibration curves made with the help of pure solutions of $CaCl_2$ and $CaSO_4$ at concentrations from 5 - 400 mg/liter coindide with each other, but the radiation from calcium as $CaHPO_4$ is considerably less over the same concentration range.

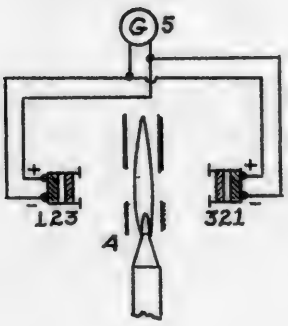

Fig. 2. Method of connecting up: 1) photo-elements; 2) light filters; 3) additional diaphragms; 4) cylindrical diaphragms; 5) galvanometer.

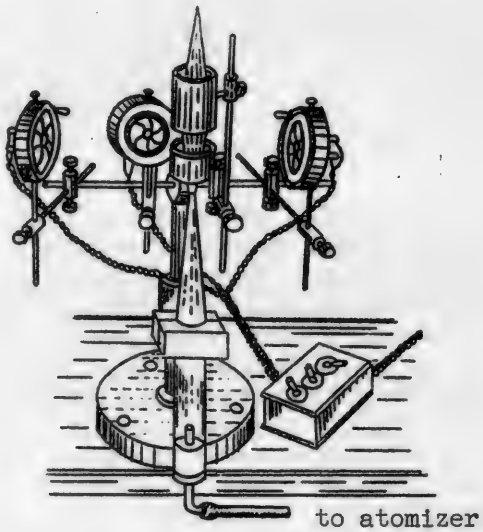

Fig. 3. General appearance of the set-up.

The relation between the radiation from calcium and the character and concentration of the acid in which the calcium salt is dissolved is of great practical interest, therefore. We took 100 mg/liter of calcium as $CaCl_2$, which was then dissolved in four acids of various concentrations. Their calcium contents were determined by means of calibration curves drawn up with the aid of aqueous solutions of $CaCl_2$. The results obtained are given in Table 1.

From these results it is evident that on increasing the concentration of H_2SO_4 and HNO_3 the radiation intensity of the calcium decreases, while in the case of acetic acid it increases; in the case of hydrochloric acid behavior is haphazard[1]). In soil analysis determinations in hydrochloric acid solutions are of practical importance. It should be pointed out that if the hydrochloric acid concentration does not exceed 1%, the analysis can be carried out using aqeous standards and vice-versa. In general the nature of the acid used and its concentration should be taken into account when carrying out an analysis.

Further tests showed that high results are obtained for calcium when sodium is present in solution. In order to avoid this, the compensation method developed above for sodium is used.[2])

1) Solutions were prepared and analyzed several times.
2) According to the location of the maximum transmission of the Ca-filter and the width of the transmission band it may be also necessary to compensate for potassium.

TABLE 1

Relation between Intensity of the Calcium Radiation and the Nature and Character of the Acid Used.

Acid Concentration	Acid			
	HCl	H_2SO_4	HNO_3	CH_3COOH
0.01N.....	104	78	87	96
0.1N.....	110	67	80	100
1N.....	93	58	73	120

It should be remembered that the concentration of sodium for which compensation is made should correspond roughly to the concentration of sodium in the test solution. Otherwise the results for calcium may be too high or too low because of the difference in the character of the transmission by the light filter for the sodium rediation as shown in Fig. 4, along the abscissa of which is plotted the logarithm of the sodium concentration, and along whose ordinate the logarithm of the galvanometer deflection is plotted. Graph 1 represents the relation of the intensity of the sodium radiation passing through the Na-filter, and Graph 2 through the Ca-filter. The point of intersection of the two curves corresponds to the point at which the photo-currents are equal and the sodium concentration at which compensation is made. It follows from this that if the sodium concentration in the test solution is lower than the concentration at which compensation is made, then the reqults for calcium will be low and vice-versa.

In practice, up to a limit of 100 mg/liter of sodium, it is possible to compensate for the effect of sodium at one sodium concentration, e. g. 500 mg/liter; the overwhelming majority of soil analyses lie within these limits, except total calcium analysis after fusion and analysis of some other specific materials. It is not essential to know the exact amount of sodium in solution; it can be determined approximately on the same apparatus.

Fig. 5 illustrates calibration curves for calcium in the presence of 10 mg/liter of sodium and for various compensation concentrations of sodium.

Table 2 contains results of the analysis of aqueous solutions of $CaCl_2$ in the presence of 10 g/liter of sodium as NaCl and Na_2SO_4. The concentration of sodium is similar to that in the solutions obtained after fusion of the soil with soda. Aqueous solutions of $CaCl_2$ were used as standards.

The results are of two fold interest:

1) The difference between the concentrations of calcium obtained with and without compensation is almost constant. In the presence of Na_2SO_4 this difference on an average amounts to 26 mg, while in the presence of NaCl it is 30 mg. The high values obtained when no compensation is made is caused by the presence in solution of sodium which gives a considerable background in the flame, and inefficient separation on the part of the Ca-filter (it is possible that the sodium salts are contaminated with calcium salts). Compensation for all concentrations of calcium is effected by subtracting equal amounts from the fictitious concentration obtained as the result of the presence of sodium ions in solution.

2) On increasing the calcium concentration there is observed a decrease in the values actually found for it and this decrease increases with relatively increasing concentration. This decrease is clearly defined in the presence of Na_2SO_4 and is also noticeable in the presence of NaCl. This phenomenon apparently depends on the nature of the anion linked with the sodium. Some results which

illustrate this point are given.

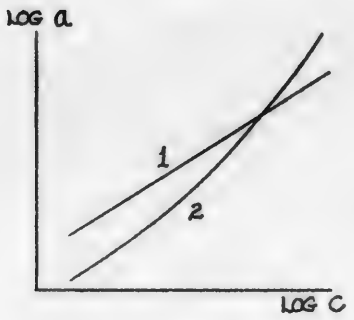

Fig. 4. Shape of the calibration curves for sodium;
1) for a Na-filter; 2) for a Ca-filter.

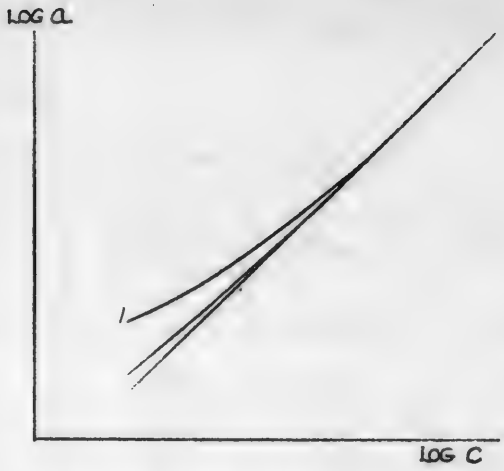

Fig. 5. Shape of the calibration curves for calcium (from 25-1000 mg/liter) in the presence of 10 g/liter of sodium.
1) Without compensation; 2) compensation at 4 g/liter of sodium; 3) compensation at 10 g/liter of sodium.

TABLE 2
Analysis of Aqueous Solutions of $CaCl_2$ in the Presence of 10g/liter of Na as NaCl and Na_2SO_4

Ca taken in the form of $CaCl_2$	Ca found in mg			
	In the presence of Na_2SO_4		In the presence of NaCl	
	with compensation	without compensation	with compensation	without compensation
Ca 5 mg/liter + Na 10000mg/l.	5.2	32.0	5.5	36.5
10 " + Na 10000 "	10.5	37.0	11.0	42.0
20 " + Na 10000 "	21.0	47.0	21.5	52
40 " + Na 10000 "	40.0	65.0	42.0	72
100 " + Na 10000 "	85.0	112.0	100.0	130
200 " + Na 10000 "	150.0	175.0	198.0	230
400 " + Na 10000 "	260.0	285.0	385.0	415

The results in Table 3 illustrate the relationship between calcium determined both as $CaCl_2$ and $CaSO_4$, and the sodium concentration; sodium is present as NaCl and Na_2SO_4.

These results show that in mixtures of $CaCl_2$ + NaCl the concentrations of calcium found agree with the original concentrations. The tendency observed earlier toward a decrease in the concentration actually found for calcium on increasing its concentration in the solution of the test mixture must not be forgotten.

In mixtures of $CaSO_4$ + NaCl, $CaCl_2$ + Na_2SO_4 and $CaSO_4$ + Na_2SO_4 there is a sharp decrease in the concentration found as compared with the initial concentration. What apparently gives rise to this decrease in the concentration determined for calcium is the presence of the SO_4^{2-} ions in the salt solution. The

maximum decrease in concentration found for calcium occurs in the presence of 2 – 4 g/liter Na. In this case there appears to be a point of inflexion which is rather interesting.

TABLE 3

Relation between Ca Determined and Na Concentration

Ca taken in mg/ml	Na added in mg/ml	Ca found in mg/ml	Ca taken in mg/ml	Na added in mg/ml	Ca found in mg/ml
As $CaCl_2$	As NaCl		As $CaSO_4$	As NaCl	
200	1,000	200	200	1,000	150
200	2,000	200	200	2,000	140
200	4,000	200	200	4,000	150
200	10,000	198	200	10,000	184
	As Na_2SO_4			As Na_2SO_4	
200	1,000	140	200	1,000	126
200	2,000	117	200	2,000	120
200	4,000	118	200	4,000	125
200	10,000	150	200	10,000	155

Results on the effects of aluminum, magnesium, and sulfuric acid [1] in solution on calcium determinations are of considerable interest. These results are given in Table 4.

The results given in Table 4 show that the intensity of the calcium radiation falls sharply in the presence of aluminum. This decrease in intensity is greater the lower the calcium concentration and the greater the aluminum concentration. There is a particularly large decrease in intensity when calcium, aluminum, and sulfuric acid or, more accurately, SO_4^{2-} ions are all present simultaneously in solution. When hydrochloric and nitric acids are added to the solution instead of H_2SO_4 the decrease is not observed.

When $CaCl_2$ and $MgCl_2$ are present at the same time the results found for calcium are somewhat high; this may be the result of the superposition of the magnesium band, or even more probably the result of contamination of the magnesium salts with calcium salts. In soil analysis any effect shown by magnesium will be absent in the overwhelming majority of analyses because of its low concentration. When materials having a high concentration of magnesium are analyzed possible interference on the part of magnesium must be borne in mind and corrected for in accordance with the actual conditions of analysis.

Further, the results in Table 4 show that the intensity of the calcium radiation when both magnesium and sulfuric acid are present in solution is strongly depressed, but to a smaller extent than when aluminum is present; the effect becomes more marked with increasing calcium concentration. We established that $MgSO_4$ in solution leads to a considerable lowering of the results for calcium determinations (these results are not given in this article).

The results given in Table 5 clearly demonstrate the special role played by Al^{3+} and SO_4^{2-} when both are present together. All the solutions are hydrochlo-

[1] The concentration of sulfuric acid is 5 ml/liter of solution.

ric solutions (HCl 8%), all the salts are hydrochlorides, the number after the symbol for the element denotes the amount of the element in mg/liter of solution. 0.2 ml of H_2SO_4 is added per liter.

TABLE 4

Effect of Al, Mg, and H_2SO_4 on Ca Determinations

Ca taken as $CaCl_2$, in mg/liter	Al added as $AlCl_3$ (+H_2SO_4), in mg/liter	Ca found, in mg/l.	Mg added as $MgCl_2$ (+H_2SO_4) in mg/liter	Ca found in mg/liter
20	500	11	1,000	23
100	500	75	1,000	104
400	500	340	1,000	400
20	500 + H_2SO_4	0	1,000 + H_2SO_4	21.5
100	500 + H_2SO_4	4.4	1,000 + H_2SO_4	95
400	500 + H_2SO_4	52	1,000 + H_2SO_4	250
200	200	165	200	200
200	500	155	400	200
200	1,000	145	1,000	205
200	200 + H_2SO_4	46	200 + H_2SO_4	115
200	500 + H_2SO_4	14	500 + H_2SO_4	130
200	1,000 + H_2SO_4	5	1,000 + H_2SO_4	165

The information given above shows that both cations and anions present in solution can affect calcium determinations. High results for calcium in the presence of sodium is a consequence of a simple superposition of the wide and intense background of sodium, the possible appearance of sodium radiation at 6154/61 A, and inefficient light filters. This may be overcome by compensation. It will be of less importance also when better light filters are used.

Low results for calcium or what boils down to the same thing, a decrease in intensity of its radiation when Al^{3+} and SO_4^{2-} ions are present, particularly when present together, owe their origin to something entirely different; the low results are related to complex physico-chemical processes occurring in the flame, and probably with the formation of new, stable molecular compounds, which depress the number of free atoms in the flame zone.

A decrease in intensity is observed not only for the calcium band at 5,500 and 6,200 A (this can be observed visually) but even for the fundamental line 4,227 A, as we established by separating this line with a monochromator and measuring its intensity with a photoelectric multiplier.

Possibly Ca^{2+} and Al^{3+} ions are oxidized in the flame to give CaO and Al_2O_3, which then react at the high temperature of the flame to give stable compounds-calcium aluminates of the type $CaAl_2O$ and $Ca_3Al_2O_4$. It is possible that SO_4^{2-} favors oxidation of the cations and formation of aluminates or other more complex and stable compounds.

That calcium and aluminum do react can be confirmed by calcining them. In the presence of sulfuric acid the reaction is considerably more rapid though the reaction product outwardly differs somewhat from that obtained in the absence of sulfuric acid.

Let us consider the analytical results for calcium in various materials. Table 6 contains results on the analysis of aqueous extracts of soils. Analysis was carried out on the basis of aqueous standard solutions of $CaCl_2$ and using the band at 6200 A. The samples contained up to 300 mg of sodium /liter. Results for calcium are practically the same with and without compensation for 100, 200, and 300 mg of sodium /liter.

TABLE 5

Effect of Cations and Anions in Solution on Ca Determinations

Ca taken, in mg/l	Element added and its amount, in mg/l	Ca found, in mg/l	Relative error, in %
100	Mg 25, Fe 50, K 40, Na 100, HCl, H_2SO_4	62	−38
200		110	−45
400		175	−56
100	Ditto + Al 150	9	−91
200		31	−84
400		140	−66

TABLE 6

Results of the Analysis of Aqueous Soil Extracts

Sample No.	Method		Deviation, in %
	Photometric.	Chemical.	
1	10.6	10.0	+ 6.0
2	24.7	26.0	− 5.0
3	26.0	27.9	− 6.8
4	29.0	32.0	− 9.4
5	30.6	32.0	− 4.4
6	70.0	66.8	+ 4.8
7	187.0	230.0	−19.0
8	191.0	248.0	− 23.0
9	276.0	269.0	+ 2.6
10	440.0	447.0	− 1.5
11	468.0	480.0	− 2.5

The mean arithmetic deviations of the results adduced is ± 8%. There is an obvious tendency toward low results for calcium. Samples 7 and 8 are extracts from salt soils containing considerable amounts of SO_4^{2-} ions. After a five-fold dilution the final results obtained were 225 and 242 mg/liter, respectively, which were in godd agreement with chemical analysis. The mean deviation is lowered to ± 4.3%.

Results which are low by as much as 25% of the calcium present were obtained during the analysis of strongly mineralized soil waters; better results were obtained when they were diluted.

Thus analysis of aqueous (and other) extracts for calcium on the basis of pure aqueous standard solutions of calcium can lead to systematically low results for calcium. The composition of the standard calcium solutions should reflect that of the test samples.

Table 7 contains results on the determination of calcium in soils fused with soda and subsequently dissolved in water. A characteristic of these solutions is the presence of large amounts of sodium (up to 10g/liter) and the acid character of the solutions (ca. 4% HCl); two types of standards were used: 1) 10g/liter of sodium (as NaCl) was added to acid solutions of $CaCl_2$ and 2) the same solutions containing Al 300, Mg 50, Fe 100, K 80 mg/liter (all chlorides). The first four samples were analyzed by means of both standards.

The results given in Table 7 show that soils cannot be analyzed for total calcium using standards of the first type (they do not correspond in composition to that of the test samples) and that accurate results can be obtained when standards with compositions approximate to that of test samples are used. Of interest is the determination of total calcium in soil after decomposition with HF (large amounts of sodium are absent). Decomposition is usually carried out in the presence of H_2SO_4. Analysis of the solution obtained gave considerably lower

results than those obtained for soils which were fused.

TABLE 7

Determination of Total Calcium in Soils After Soda Fusion

Sample No.	Method		Deviation, in %	Notes
	Photometric	Chemical		
1	5.1	8.1	-37.2	First type of standard
2	5.4	8.6	-37.0	
3	5.5	9.1	-39.3	
4	6.0	10.0	-40.0	
1	8.5	8.1	+ 4.9	Second type of standard
2	8.5	8.6	- 1.2	
3	9.2	8.1	+ 1.1	
4	10.0	10.0	0	
5	8.0	8.0	0	
6	8.4	8.3	+ 1.3	
7	8.7	8.1	+ 7.8	
8	8.9	8.9	0	
9	7.8	7.5	+ 4	

TABLE 8

Results of Calcium Analyses of Plant Ash

Sample No.	Method		Deviation, %
	Photometric	Chemical	
1	5.7	5.1	+11.8
2	8.2	8.5	- 3.4
3	9.2	9.5	- 3.2
4	16.5	15.5	+ 6.5
5	21.7	21.1	+ 2.9
6	18.6	19.2	- 3.1
7	22.5	21.1	+ 3.6
8	7.4	7.7	- 3.9
9	9.1	9.6	- 5.2

Decomposition in the presence of HCl takes very long and is difficult. Here it is also possible to get incomplete decomposition and the formation of very stable compounds of CaF_2. Results of chemical analysis of solutions obtained by this method were so conflicting that they could not be compared with results obtained photometrically.

Table 8 contains results on the calcium content of plant ash. The plants were ashed and the ash washed with dilute HCl; after dilution a weak acid solution was obtained. Analysis was carried out using aqueous solutions of $CaCl_2$ as standards.

These results show that plant ash can be analyzed for calcium using aqueous $CaCl_2$ standards. For this type of analysis the sodium content was so low that there was no need for compensation. One must however bear in mind the possibility of a large increase in the amount of some elements in plant ash because of the plants' selective action and the large amounts of certain elements in soils and fertilizers. In such cases the standard solution must have a composition similar to that of the test solutions and compensation may be essential.

SUMMARY

1. By means of a flame-photometric method calcium can be determined in solution by means of its characteristic radiation at 6200 and 5500 A, the radiation being isolated by interference light filters. When a selenium photoelement is used the sensitivity of the method is considerably greater for the first band than for the second.

2. Pure $CaCl_2$ and $CaSO_4$ solutions of equal concentration give equally intense radiation. The radiation from calcium as $CaHPO_4$ in solutions of the same calcium concentration is considerably smaller.

3. The accuracy of calcium determinations depends on the other cations and anions present in solution. There is a considerable decrease in radiation intensity for calcium when both Al^{3+} and SO_4^{2-} are present in solution. Interference from sodium can be compensated for.

4. The concentration of sodium at which compensation is carried out should approximate to the concentration of sodium in the test solution.

5. The composition of synthetic standards must approximate as closely as possible to the composition of the test solution.

Solution with various calcium concentrations established by chemical methods should be used as standards.

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QUANTITATIVE COLORIMETRIC DETERMINATION OF ALIPHATIC ALCOHOLS IN THE ULTRA VIOLET

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The problem of determining aliphatic alcohols quantitatively at low concentrations has not yet been satisfactorily solved. Most of the methods published for the quantitative determination of alcohols are only applicable at conentrations of 10^{-3} - 10^{-2}% and higher.

Thus quantitative determination of alcohols by oxidation with potassium bichromate or permanganate [1-4], is only possible at alcohol concentrations greater than 10^{-2}% and the accuracy is not very good at that, since calculation of alcohol content is based on the equation:

$$3R\cdot CH_2OH + 8H_2SO + 2K_2Cr_2O_7 = 3R\cdot COOH + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O.$$

Further oxidation of the acids obtained is ignored [5]. Moreover the analysis is complicated by the presence of other materials of a reducing nature [2].

The sensitivity of Fischer's [6], and Pondorf's [7], methods respectively do not exceed 10^{-2}%. Ketslakh and Pigulevsky [8], noted when using their methods considerable deviations in reaction velocities for the formation of alkylnitrites of various aliphatic alcohols, which hinder the application of the methods for analysis of mixtures containing a mixture of several alcohols.

Zerevitinov's method [9], is applicable for alcohol concentrations of 10^{-3}% and higher; it can, however, only be used for the analysis of absolutely dry materials.

Verley's method [10], which is based on acetylation of the alcohols is only applicable for concentrations of alcohol from 10^{-2}% upwards.

The most sensitive methods for the quantitative determination of alcohols are Vorokhobin's method [11], according to which the alcohol is oxidized with potassium bichromate and the test solution colorimetrically measured by means of the green color of trivalent chromium, and Nizovkin's colorimetric method [12].

Vorokhobin's method according to the author himself permits quantitative determination of ethyl alcohol at concentrations of $5\cdot10^{-4}$%, upwards and requires careful purification of the test material from all reducing material. Nizovkin's method is applicable to the analysis of test material containing ethyl alcohol in amounts greater than 10^{-4}%; it is however very complicated and considerable losses of alcohol are possible.

In the present investigation we have attempted to use absorption in the ultraviolet by the alkylnitrites formed as the result of the reaction between alcohol and nitrous acid according to the following equation:

$$ROH + HNO_2 = RNO_2 + H_2O.$$

For the quantitative determination of alcohols, Thomson's [13], and Goodeve's [14], results indicated that gaseous aliphatic alkyl nitrites have a clearly defined absorption spectra in the near ultra-violet consisting of narrow bands at 390, 365, 355, 345, 323, 320 mμ. The position of the bands according to Thomson and Goodeve depend to only an insignificant extent on the chemical nature of the radical R.

Measurements which we made on the absorption spectra of ethyl nitrite, propyl nitrite, and octyl nitrite dissolved in gasoline on the SF-11 spectrophotometer showed that the forms of their spectra is independent of the nature of the radical. All the alkyl nitrites mentioned have a wide absorption band at 400-320 mμ, with maxima at 380, 355, and 345 mμ.

The shape of the absorption curves obtained for the alkyl nitrites shown in Fig.1 and the appreciable value of the absorption coefficient which is $10^2 cm^2/mol$ at 355 mμ indicate that the use of absorption spectra of the alkyl nitrites for colorimetric determination of alcohols is sound. Experiments were accordingly carried out on the colorimetric determination of aqueous solutions of the following alcohols: methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, n-octyl- alcohols, and methylhexylcarbinol, using the following technique; test material containing the alcohol is treated with nitrous acid and the alkyl nitrite formed extracted with gasoline; the extract is placed in a cuvette with quartz windows and then colorimetric determinations carried out with a differential adsorptiometer designed for working in the ultra-violet [15].

Standards were prepared by dissolving aliquots of the alcohols in water using ampoules weighed to an accuracy of 0.02 mg. The alcohols were distilled beforehand and dehydrated, either over freshly calcined copper sulfate or over potash and then distilled over metallic calcium.

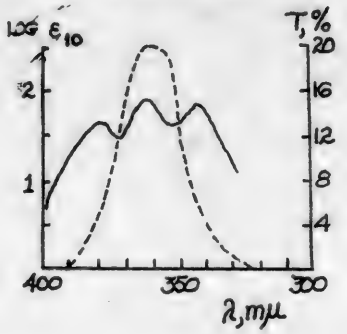

Fig.1. Absorption curve for alkyl nitrites dissolved in gasoline, solid line. Transmission curve for the filter, broken line. T,%- light filter transmission in %. ϵ_{10}, molar absorption coefficient for the alkyl nitrites.

Tests were prepared for colorimetric determination as follows: 20 ml of aviation gasoline (washed several times with sulfuric acid d = 1.84 and distilling in the range 35-100°) was introduced into a 50-60 ml separating funnel; this was followed by 20 ml of test solution and 1 ml of 5 N HCl.

2 ml of 25% aqueous sodium nitrite was then added rapidly to the contents of the funnel by means of a pipet with a wide tip, the funnel was then stoppered and shaken thoroughly for 5 minutes.

When the two layers had separated the water was run off while the upper gasoline layer containing the alkyl nitrite was run into a second separating funnel containing 20 ml of aqueous 10% sodium bicarbonate (or 0.1 N NaOH). After a 5 minute period of shaking to free the gasoline layer of alkyl nitrite from nitrogen oxides, the gasoline was rapidly transferred to a cylindrical cuvette with quartz windows and a colorimetric determination carried out using a cuvette filled with pure gasoline as a standard.

In all our experiments we used water-cooled funnels to cut down as much as possible any loss of volatile alkyl nitrites.

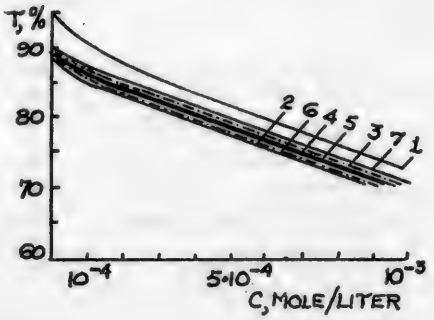

Fig.2. Calibration curves for alcohols:
1- CH_3OH; 2- C_2H_5OH; 3- n-propyl alcohol; 4- isopropyl alcohol; 5- butyl alcohol; 6- isobutyl alcohol; 7- n-octyl alcohol; T%- transmission of solution in % (thickness of layer 2 cm).

The solutions were colorimetrically determined using light filters operating at 360 mμ [16].

The transmission curve of the light filter used is compared with the absorption curve of the alkyl nitrites on Fig. 1.

Calibration curves for solutions of some of the alcohols we tested are given in Fig. 2. The cuvette length was 2 cm both for drawing calibration curves and for analyzing test samples.

As shown in Fig.2 the calibration curves lie close to each other, being arranged on both sides of the curve for n-butyl alcohol. The only anomalous behavior is shown by methyl alcohol; this is probably the result of loss of methyl nitrite on account of its high volatility. Results for the analysis of aqueous solutions of the alcohols listed above are given in Tables 1 and 2.

TABLE 1

Alcohol taken in %	Alcohol found in %	Δc/c in %
Methyl alcohol		
0.0200	0.0202	1
0.0116	0.0110	6
0.0085	0.0086	1.5
0.0058	0.0058	0
0.0030	0.0032	7
0.0022	0.0023	5
0.00085	0.00080	6
Ethyl alcohol		
0.0360	0.0354	2
0.0225	0.0224	0.5
0.00900	0.0096	7
0.00570	0.00530	7
0.00190	0.00175	8
0.00095	0.00085	10.5
0.00080	0.0007	12
n-Propyl alcohol		
0.00605	0.00605	0
0.00403	0.00400	1
0.00200	0.00195	3
0.00150	0.00151	1
0.00130	0.00125	4
0.00110	0.00113	3
0.00060	0.00065	9
0.00050	0.00060	20
Isopropyl alcohol		
0.0375	0.0370	1.5
0.0100	0.0096	4
0.0066	0.0062	7
0.0020	0.0019	5
0.00125	0.00130	4
0.00089	0.00080	11
0.00050	0.00043	14
0.00025	0.00030	20

TABLE 2

Alcohol taken in %	Alcohol found in %	Δc/c in %
n-Butyl alcohol		
0.0300	0.0293	2.5
0.0130	0.0135	4
0.0090	0.0092	2
0.0056	0.0054	4
0.0033	0.0030	10
0.0022	0.0024	9
0.0050	0.0058	16
Isobutyl alcohol		
0.00467	0.00450	3.5
0.00311	0.00300	3
0.00175	0.00170	3
0.00117	0.00105	10
0.00100	0.00089	11
0.00087	0.00080	9
0.00035	0.00029	17
0.00025	0.00027	10
n-octyl alcohol		
0.0317	0.0320	−1
0.0096	0.0090	7
0.0053	0.0048	9
0.0031	0.0032	0
0.0016	0.0015	6
Methylhexylcarbinol		
0.00320	0.00285	11
0.00181	0.00170	6
0.00160	0.00165	3
0.00145	0.00154	6
0.00103	0.00096	7

These results show that when the layer of solution of alkyl nitrite used for colorimetric determination is 2 cm thick, determination can be carried out with a relative error of 1-20%. Quantitative determination can be carried out right down to 10^{-3} - $5 \cdot 10^{-4}$%. A determination takes 20-25 minutes.

Sensitivity can be increased by increasing the thickness of the solution under examination and by cutting down the volume of extractant.

As pointed out above the calibration curves for the various alcohols tested are closely grouped round the curve for n-butyl alcohol. This fact indicates that it may be possible to use the calibration curve for butyl alcohol as a general mean calibration curve for all the alcohols tested; this of course means a

reduction in accuracy, but nevertheless may still be good enough to give an idea of the total content of alcohols in solution.

To check this possibility we carried out analysis of several mixtures of alcohols. Results are given in Table 3.

TABLE 3

Experiment No.	Designation of alcohol	Alcohol taken: Concentration of alcohol in mol/liter	Alcohol found in mol/liter	c/c in %
1	Ethyl	$2.35 \cdot 10^{-4}$	-	-
	Isopropyl	$2.72 \cdot 10^{-4}$	-	-
	Isobutyl	$3.10 \cdot 10^{-4}$	-	-
	Total	$8.17 \cdot 10^{-4}$	$7.23 \cdot 10^{-4}$	11
2	n-Propyl	$1.24 \cdot 10^{-4}$	-	-
	Isobutyl	$0.73 \cdot 10^{-4}$	-	-
	n-Octyl	$2.91 \cdot 10^{-4}$	-	-
	Total	$4.88 \cdot 10^{-4}$	$4.15 \cdot 10^{-4}$	15
3	Ethyl	$2.35 \cdot 10^{-4}$	-	-
	Isopropyl	$1.36 \cdot 10^{-4}$	-	-
	n-Butyl	$0.72 \cdot 10^{-4}$	-	-
	n-Octyl	$1.91 \cdot 10^{-4}$	-	-
	Total	$6.34 \cdot 10^{-4}$	$7.66 \cdot 10^{-4}$	21

SUMMARY

1. The possibility has been demonstrated of carrying out colorimetric determination of aqueous solutions of the following alcohols in the ultra-violet: methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl isobutyl-, n-octyl-alcohols and methylhexylcarbinol. The relative error of determination is 1-20%. The sensitivity of a determination is 10^{-3} - $5 \cdot 10^{-4}$% alcohol in the test material.

2. It has been established that the shape of the calibration curves for the alcohols listed with the exception of methyl alcohol permits quantitative evaluation of the total alcohol content in one solution with a relative error of 11-21%.

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2) See Consultants Bureau Translation, p. 23.

QUANTITATIVE MICRO-DETERMINATION OF CARBON, IN PARTICULAR IN TANTALUM CARBIDE

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A. A Micro-method for Determination of Total Carbon.

Carbon is usually determined quantitatively either gravimetrically, by trapping the gases evolved in absorption flasks filled with askarite and other similar reagents, or gas-volumetrically, using an Orsat type of apparatus. For very accurate gravimetric methods of determining small amounts of carbon, a micro-balance has to be used.

Our aim was to develop a method of determining small amounts of carbon in which an ordinary analytical balance could be used without sacrifice of accuracy, but rather with greater accuracy; this we hoped to achieve by using a method of micro-gravimetric titration worked out by one of us [1].

Acidimetry can be used as a basis for determination of carbon. In our case, however, the problem is complicated by the fact that before titration the CO_2 must be completely removed from the gas mixture after combustion which contains oxygen. We used a standard solution of barium hydroxide to absorb the CO_2; the amount of CO_2 absorbed is determined by back titration of excess barium hydroxide with 0.1 N hydrochloric acid, using phenolphthalein as indicator, the barium carbonate formed being removed beforehand.[1)]

10 mg of carbon is equivalent to 37 mg CO_2; the accuracy possible, therefore, when an ordinary analytical balance is used for gravimetric determination, is ca. 0.5% because of weighing errors. When only 1 mg of carbon is available the accuracy does not exceed 5%.

When a volumetric finish is used 10 mg of carbon is equivalent to 16.6 ml of 0.1 N hydrochloric acid, which can be measured with an accuracy of one drop (0.02 - 0.05 ml), i.e. 0.15 - 0.2%. For smaller amounts of carbon, down to 1 mg C, the same accuracy can be maintained by using weaker standard solutions (0.01 N), or using micro volumetric and particularly ultra-micro gravimetric apparatus.

A combination of these techniques permits determinations of the same order of accuracy with tenths of a milligram of carbon.

This simple method has great possibilities when the carbon content is appreciable, particularly in alloys. A sample of the order of ca. 100 mg can be weighed out accurately enough on a simple analytical balance and its carbon content (ca. 1 mg) can be determined with great accuracy. When such a technique is used it is essential that the gas evolved should be completely absorbed by the standard solution. The use of small porous glass sinters to give a fine stream of bubbles is inadmissible because of the difficulties involved during subsequent titration (and also because of clogging of the pores with barium carbonate); the use of flasks of the Tishchenko and Drexel type does not ensure complete CO_2 absorption when weak solutions are employed.

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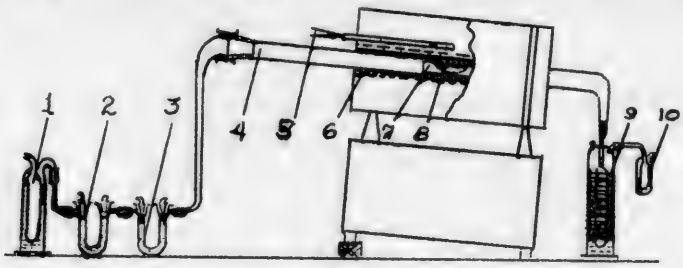
1) Many authors recommend back titration with oxalic rather than hydrochloric acid (in order to avoid partial solution of barium carbonate in cases where there is poor mixing and the local hydrogen ion concentration is sufficient to dissolve the carbonate when hydrochloric acid is used).

We constructed an absorption apparatus (see following article) [2], with a plate type absorption system, each section of which keeps the bubbles in contact with the absorbent solution, and is far more efficient than scrubbers of the Drexel type. The precipitate which forms falls on the plate without blocking the openings. Titration of the solution in this flask presents no difficulty.

The Apparatus Used.

The set-up is schematically shown in the diagramm. Oxygen from a reservoir passes into two flasks connected in series containing sulfuric acid; these are connected to two tubes filled with powdered BaO (KOH, NaOH) and to a tube filled with phosphorus pentoxide. The oxygen next passes into a quartz tube fitted into a combustion oven. Oven and combustion tube are inclined so that the CO_2 flows out into the absorbent side of the apparatus. The quartz tube is connected with the specially constructed scrubber containing absorbent solution for trapping the CO_2 which passes through it with oxygen after combustion. Where necessary the gas can be passed first through an absorbing tower filled with phosphorus pentoxide in order to trap and determine moisture. A standard solution of barium hydroxide (see below) is poured beforehand into the scrubber, which is filled with an inert gas such as argon or oxygen. From this scrubber, the gas proceeds to a control scrubber filled with $Ba(OH)_2$, where the gas is finally tested to see whether or not it is free of CO_2.



1-Scrubber with H_2SO_4; 2- tube with BaO; 3- tube with P_2O_5; 4- quartz tube; 5- platinum-platinum rhodium thermocouple; 6- Mars oven; 7- protective quartz tube; 8- porcelain boat; 9- scrubber with $Ba(OH)_2$; 10- control flask with $Ba(OH)_2$.

Micro Determination of Carbon

The aliquot of carbon-containing material, e.g. graphite, is weighed into a porcelain boat and heated for 19 minutes to the temperature of incipient combustion, in the case of graphite to 600-650°. The amount of oxygen passed through the combustion tube should be approximately four times that of the CO_2 formed. Dilution should not be greater than this during the course of combustion. 20 mg of graphite yields ca. 40 ml of CO_2, so that approximately 160-200 ml of oxygen should be fed into the combustion tube. Oxygen should not be passed into the tube from the reservoir while the temperature is being taken up to 600°, since the amount of it already in the oven should be enough to start off the combustion of graphite (the volume of the tube is 150-200 ml under normal conditions). When the temperature approaches 600°, or even before, the oxygen throughput must be controlled (i.e., the oxygen passing through the scrubbers containing sulfuric acid into the oven) so that it is ca. 3 ml/min. During the subsequent 10 minutes the temperature is raised to 900-950° and is kept at this level during combustion. The oxygen throughput remains unchanged for the first 30-40 minutes and only after the formation and washing of considerable amounts of barium carbonate can the rate be increased to, say, 5 ml/minute. The oven is then switched off and the oxygen passed through at a rate of 20-25 ml/minute for 5-10 minutes to expel

any residual CO_2. The scrubber is disconnected from the combustion tube and a tube for leading in oxygen free from CO_2 connected to its inlet tube. The control flask containing $Ba(OH)_2$ is also disconnected and the outlet tube closed with a glass stopper, etc. The cork of the tube used for leading in the buret tip is then removed and an inert gas passed through; two drops of phenolphthalein are then added and the tip of the buret containing standard HCl introduced. The throughput of the inert gas should be as low as possible; the solution is thereby mixed during titration with HCl in such a way that the solution in the upper part of the titration flask is not colorless, thus indicating that it is not acid and thereby avoiding the danger of $BaCO_3$ dissolving in the HCl and giving erroneous results. If mixing is too rapid as a result of too high a gas throughput there may be mechanical carryover of solution and subsequent errors. The optimum inert gas throughput can be determined in a preliminary experiment. The optimal value can then be easily attained by counting the gas bubbles in the washer, while the color of the indicator in the upper layer serves as a guide[1]. The whole titration usually takes only 15-20 minutes. The acid is added at the rate of 1 ml/minute during the first half of the titration, and more slowly as the end point is reached.

Graphite with a moisture content of 1% was used as test material. The aliquots of carbon used for work with washer No.3 varied from 20-35 mg. The concentration of the barium hydroxide and hydrochloric acid used was 0.2 N. Analytical grade hydrochloric acid was standardized gravimetrically by precipitation of 50 ml of the solution with excess silver nitrate. The accuracy of determination was 0.01%. Barium hydroxide was standardized by titration in an argon atmosphere.

TABLE 1

Determination No.	Weight of carbide	Total carbon found		Ta found from the difference between (2) and (3) calculated as %	Ta_2O_5 found after combustion, in mg	Ta found in the aliquot after calculation from the amount of Ta_2O_5		Mean amount of Ta from (5) and (8), in %	Overall formula
		in mg	in %			in mg	in %		
1	2	3	4	5	6	7	8	9	
1	196.1	10.7	5.45	94.55	227.0	185.9	94.79	94.67	-
2	188.4	9.7	5.20	94.80	218.5	178.9	94.93	94.86	-
3	152.2	7.9	5.19	94.81	174.7	143.0	93.95	94.38	-
		Mean 5.28 ± 0.11				Mean 94.63 ± 0.17			$TaC_{0.84}$

Note. Ta was determined both from the pentoxide formed and from the difference TaC_x (aliquot) − C_{total}.

Experiments showed that the accuracy is limited only by the accuracy with which the graphite is weighed; for graphite weighing 10-30 mg the accuracy lies within the limits of 1% of the weight.

[1] Toward the end of the titration one should cease adding acid from time to time for about half a minute, in order to detach the flask from the buret and, while still passing inert gas through, incline the flask from side to side. When this is done the gas lifts the precipitate off the bottom and stirs up the alkaline layer with the layer on top of it. Slight shaking of the absorption flask will also facilitate this.

For determination of carbon in various compounds and alloys it is expedient to carry out one or two qualitative tests to establish the initial and final combustion temperatures of the materials in oxygen and the optimum rate and amount of oxygen to be passed through the apparatus.

Ca. 200 mg of tantalum carbide was used for determination of total carbon. Combustion and titration were carried out as described above. Results are given in Table 1.

Ultra-Micro Gravimetric Determination of Carbon.

In some instances it is necessary to determine very small amounts of carbon. E.g. the determination of free carbon in tantalum carbide. Having taken a sample of 30-40 mg and separated the combined carbon by a method described below, we filtered off the free carbon, the amount of this came to about 0.2% of the sample, i.e., approximately 100 γ, and in no instance greater than 1 mg. In this case the technique should be modified as follows; the combustion tube used should have a volume of 40-50 cm^3; under no circumstances should rubber connections be used.

Before combustion it is essential to ensure that all carbon dioxide has been desorbed from the tube walls by blowing through oxygen heated to 800° in an oven. This operation decreases titration errors for C (as CO_2) to 40 γ. When the tube has been thus treated the oven is moved on to the boat and combustion carried out as usual. It is essential to carry out blank tests with an empty boat because desorption of CO_2 can be observed here again, although to a smaller extent. In our experiments this amounted to 20 γ, so that a constant correction must be applied.

In order to trap CO_2 released by the combustion of 1 mg or less of carbon we made a special washer (see following article) suitable for ultra-micro gravimetric determination. 1-1.5 g of 0.1 R solution of barium hydroxide which was weighed on an analytical balance[1], was introduced into the washer and after CO_2 absorption titrated with a solution of 0.1 R HCl (where 0.1 R is a gravimetrically standardized solution as distinct from 0.1 N) by means of a gravimetric micro-buret described in [1].

B. A Micro Method for the Determination of Free Carbon in Tantalum Carbide.[2]

A mixture of hydrogen fluoride and nitric acid was used to dissolve the tantalum carbide. Normally a solution containing a high percentage of hydrogen fluoride is used, but this may give rise to some difficulties when carrying out the analysis.

We tried to find the minimum concentration of HF and the minimum ratio of $HF:HNO_3$ which would ensure that solution of the carbide would be rapid and complete.

As a result of our investigations we developed the following micro method. 30-50 mg of tantalum carbides [3], from $TaC_{0.38}$ to $TaC_{0.82}$ containing 2-6 weight % (i.e. 1-2 mg) of total carbon and approximately 0.2 to 0.8% (i.e. 0.1 - 0.4 mg) free carbon is weighed out into an 8 ml platinum crucible and wetted with 0.5 ml of water; 1 ml of a mixture of chemically pure undiluted hydrogen fluoride and nitric acid (in a ratio of 1:5) is then added. The crucible is heated on a water bath for 15 minutes, whereupon the combined carbon (carbide) dissolves completely. The crucible is then almost

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1) The theoretical basis and the technique of gravimetric titration have been developed in Ormont's article. [1].

2) Yu. K. Egorova participated in this work

filled with distilled water, a quartz filter stick is placed in the liquid surface, and the liquid sucked up by means of a water pump.

The concentration of hydrogen fluoride is too low to attack the quartz filter seriously, and such a filter does away with the use of asbestos filters which can be a source of large errors. The crucible is filled up again with hot distilled water and the liquid filtered off. Washing is continued to neutral reaction, after which the crucible together with precipitate and filter in which some of the carbon is stuck are dried in an oven; all the latter are then heated in a tubular combustion oven and the CO_2 evolved absorbed in 0.2 N barium hydroxide as described above.

It is best to determine carbon in such small amounts by the method of gravimetric ultra-micro titration [1].

It was established that free graphite is practically insoluble in the HF + HNO_3 mixture, and that in any case the decrease in free carbon content as a result of interaction with reagent does not exceed 1% of the absolute amount; the latter amounts to 10% of the total carbon. For an average total carbon content of ca. 5% in a sample, the amount of free carbon present does not exceed ca. 0.5%.

This method is accordingly capable of giving a high overall accuracy, of the order of $\pm$ 0.01 mg of free carbon. Thus, even for a free carbon content of the order of 0.1 mg the mean error amounts to $\pm$ 10%.

Example. A mixture of carbide plus excess carbon was taken. The total carbon found was 5.28 $\pm$ 0.11%

The results obtained for the determination of free carbon are adduced in Table 2.

TABLE 2

Experiment No.	Weight of carbide taken, in mg	Amount of free carbon found		Amount of free carbon corresponding to a mean of 0.26%, in mg	Δ - difference between C_{free} in columns (3) and (5), in mg
		in mg	in %		
1	2	3	4	5	6
1	42.5	0.114	0.27	0.111	-0.003
2	41.1	0.119	0.29	0.107	-0.012
3	40.8	0.089	0.22	0.106	+0.017
		Mean	0.26 $\pm$ 0.02%	Mean	+ 0.011

The results given in Table 2 show that the percentage error in the example given does not exceed $\pm \frac{0.011 \cdot 100}{42.5}$ = 0.02% of the weight of the carbide and $\frac{0.011 \cdot 100}{2.5}$ of the weight of total carbon.

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1) See Consultants Bureau Translation, p. 405 (this issue).

AN APPARATUS FOR THE QUANTITATIVE ABSORPTION OF GASES

B.F. Ormont and V.I. Smirnova

We have constructed a scrubbing apparatus of the types shown in Figs. 1 and 2 by means of which gases can be absorbed completely in solution and the solution subsequently used for gravimetric or volumetric determination of the gases.

The basic features of the scrubber are bells with gas outlets on top. The diameter of the opening is chosen in accordance with the experimental conditions. In the type used for CO_2 determination by absorption with barium hydroxide, the lower bells have an opening with a diameter of 2-3 mm while the diameter of the upper opening is 1-2 mm.

The apparatus shown in Fig.1 consists of individual bells fitted on to a tube which leads in the gas, and which itself ends up in a bell. Similar bells are mounted on top of each other ensuring good filling of the space between the plates (up to 10-12 bells in a length of 100-200 mm); the number of bells may be varied depending on the height h of the center tube.

The apparatus shown in Fig.2 is built on the same principle as that shown in Fig.1, but the tube on which the bells are mounted widens out in this case at its lower end and is filled with rings made from bits of thin glass tubing. This type scrubber has a number of advantages. When the gas is passing through, a large part of the solution is forced out by the gas from the inside and consequently even when small amounts of liquid are used the same effective height as that obtained with the apparatus shown in Fig.1 can be attained. The part of the solution left in the rings also participates actively in gas absorption. When absorption is carried out in this type of apparatus it is possible from time to time to stop the input of gas into the scrubber for an instand to create a higher pressure on the outlet side. This means that gas can proceed into the inside of the scrubber and leads to repeated soakings of the rings with solution. If any precipitate should form it falls onto the bottom of the scrubber through the wide openings into the lower part of the inner tube. In such cases, the lower bell should be at a distance of 15-25 mm from the bottom of the scrubber, which is sufficient for accommodating the precipitate.

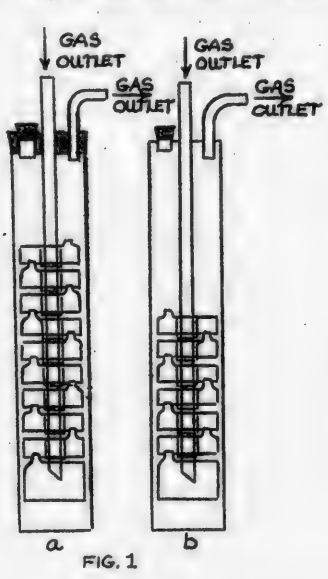

FIG. 1

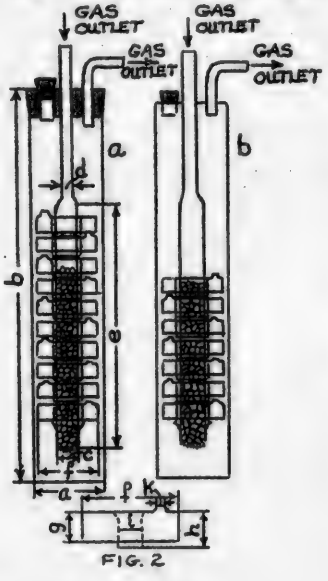

FIG. 2

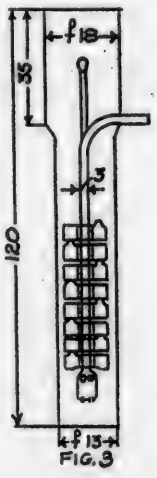

FIG. 3

Fig.1 Scrubber of the 1st type.

Fig. 2. Scrubber of the 2nd type. Number of plates, 10-12; g = 8-10 mm; h = 9-10 mm; i = C + 2 mm; k = 2-3 mm for lower and 1-2 mm for upper plates.

Fig. 3. Scrubber for microgravimetric analysis.

These scrubbers operate on the principle that the gas in broken up into small bubbles which are in contact with the absorbent solution for a long time. In some cases, e.g. absorption of CO_2 with barium hydroxide, a foam is formed which accumulates under the bells and to some extent on the surface of the solution; this also favors absorption.

Mixing of the solution by the gas passing through is very thorough even for a low overall gas throughput. This is a result of the fact that some of the gas has to accumulate on the plate before it can go through the openings.

For scrubbers of the type shown in Fig.2 which are used for CO_2 titration, standard sizes are given (in mms, see Table).

The tube leading into the scrubber may be fused in at its top end (Fig.1b, and Fig. 2b) or fitted with a rubber bung (Fig.1a, and 2a).

Of course, the gas could also be led into the bottom of the flask under the bells arranged on top of each other.

TABLE

Scrubber No.	a	b	c	d	e	f	h	V in ml
1	20/18	150	10/9	6/5	80	17/16	9	10-12
2	27/35	200	14/12	7/6	120	20/20	10	30
3	31/28	250	16/14	7/6	140	24/22	12	50

Note. The fraction sign denotes the outer and inner diameters, respectively, e.g. 20/18 means outer diameter 20 mm and inner diameter 18 mm. The volume of absorbent solution is given in ml (V).

For ultra-micro gravimetric titrations the apparatus is modified; the dimensions of the apparatus are much smaller (Fig.3), the total volume up to the top of the last plate is not greater than 4-5 ml; the top part is widened out so that the gas can leave more easily and a buret tip can be introduced. A glass rod with a sphere on one end is fused internally into the gas tube leading in the gas. By touching this rod with the buret tip a drop of any size can be taken off. The part of the drop falling on the rod remains inside the scrubber, and does not spread on the vessel walls and to other parts of the apparatus. In such a set-up there is no need for a titration stick.

Using the technique of gravimetric micro titration with 0.1 N HCl from a buret containing up to 1 g of solution, the minimum amount of HCl that can be taken is 10 mg which corresponds to 6γ of carbon.

With such high sensitivity it is possible to detect CO_2 of extraneous origin (e.g. CO_2 desorbed by the apparatus walls).

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POLAROGRAPHIC DETERMINATION OF NITRATES AND NITRITES IN SALTS AND BRINES USED FOR MEAT PICKLING.

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Heyrovsky and Nejedly [1], were the first to study the polarography of nitrites; they found that they are not reduced in neutral and alkaline electrolytes. Only after acidification of the solution did they find a wave at $E^{1}/_{2} = -0.77$ V (with respect to the normal calomel electrode), which was characteristic of the reduction of nitric oxide, and which permitted determination of nitrite down to concentrations of 10^{-5}N. Heyrovsky and Nejedly concluded that five electrons are involved in the reduction of NO, and that ammonia is the reduction product.

Subsequently Prat [2], Ruzicka [3], Tokuoka [4,5], and Tokuoka and Ruzicka [6], studied nitrates and nitrites polarographically. When LiCl or tetramethylammonium chloride were used as supporting electrolytes, respectively, reduction of NO_3^- and NO_2^- ions was observed at much more negative potentials. On adding multivalent cations (activators) to the test solution, displacement of the reduction potentials for nitrates and nitrites to more positive values was observed. Tokuoka and Ruzicka established that the diffusion current for nitrates and nitrites depends on the concentration of lanthanum chloride. Quantitative determination of NO_3^- and NO_2^- is possible when the $LaCl_3$ concentration is 50 times that of nitrate or nitrite; after improvements by other authors [7-12], this method was used for various practical purposes [13-16].

A new method of getting a wave for nitrate ions is to take polarograms in the presence of traces of uranyl salts. This method was proposed by Kolthoff and coworkers [17]. The "uranyl" method, which has since been used by other authors [18], for the determination of nitrites, has many advantages over the "lanthanum" method. Masek [19], on the basis of his critical examination of the problem, proposed that the lanthanum method, which is widely used in industry, be rejected, and that nitrates and nitrites be determined polarographically by the uranyl method.

Ingram [14], attempted to determine nitrates and nitrites in pickling brine polarographically. For nitrate determination he used a brine solution diluted 1000 times in a solution of 0.1 M $CeCl_3$ to which was added a mixture of 0.1 M $CeCl_3$, 0.001 M KNO_3 as standard. Working with Ce^{3+} salts however presents some difficulties; just as with La^{3+}, the polarographic waves for nitrate and nitrite, which are not themselves clearly defined, fuse into the current caused by deposition of alkali metals, and the results obtained are accordingly unreliable.

This paper of Ingram's was the basis of our attempt to develop the polarographic method further.

EXPERIMENTAL AND RESULTS

Kolthoff's method [17], which is used for the determination of nitrates was first of all experimentally checked; the normal salt $UO_2(CH_3COO)_2.2H_2O$, however, was used instead of UO_2Cl_2. The graph in Fig.1 shows the two waves for uranyl ions at a concentration of 10^{-3} M UO_2^{2+}; the half wave potentials of the two waves occur at -0.181 V and at -0.909 V respectively.[1)]

[1)] All potentials are referred to the saturated calomel electrode.

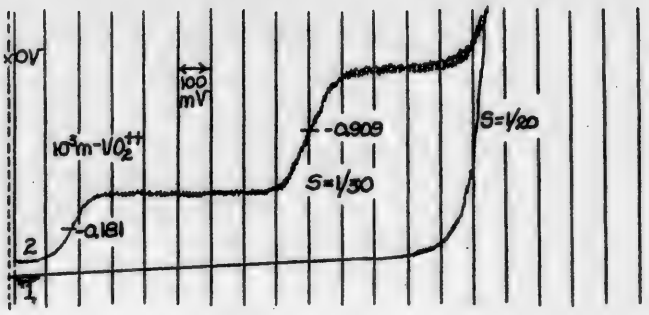

Fig.1

Uranyl Waves. Curve 1 - was taken with 4.5 ml of a solution of 10^{-1} M KCl 10^{-2}M HCl; starting at 0 V and with a sensitivity of 1/20. Curve 2 was taken with the same solution but 0.5 ml of aqueous uranyl acetate was added; the sensitivity in this instance was 1/30. A Kalousk cell with a saturated calomel electrode was used in a nitrogen atmosphere, the voltage being supplied from a 2V accumulator.

It was found that in the solution of 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$ on addition of nitrates in a concentration of $1.90 \cdot 10^{-5}$ to $1.38 \cdot 10^{-3}$ M KNO_3 there was an increase in the polarographic wave at -0.9 V. On increasing the nitrate concentration, its half-wave potential was shifted to more negative values. For the range of concentration just given these shifts amounted to -0.9 to -1.1 V (Fig.2).

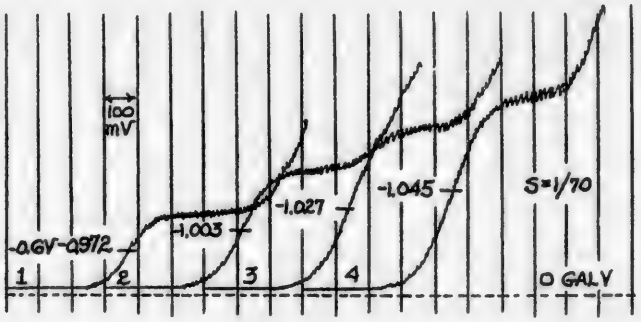

Fig.2

The Linear Relation between Limiting Current and Nitrate Concentration. To 5 ml of the supporting electrolyte 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$ was added some more of the same solution (0.1-0.4 ml) but containing 10^{-2} M KNO_3; in addition polarograms were taken starting from -0.6 V. The NO_3^- concentration for each curve was: 1 - 1.90; 2 - 3.80; 3 - 5.70; 4 - $7.40 \cdot 10^{-4}$ M KNO_3. The cell used was the Kalousk type with a saturated calomel electrode; electrolysis was carried out in a nitrogen atmosphere using a 2V accumulator as voltage supply and a sensitivity of 1/70.

Nitrites were studied in the same way. Using the same base electrolyte, they were found to be reduced at the potential of the second uranyl wave. The half-wave potential of the first uranyl wave was measured in a solution of 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$, 10^{-4}M KNO_2, and was found to be -0.181 V, while the potential of the second uranyl wave which coincided with that of the nitrite ions was found to be -1.018 V. Using the same base

electrolyte but at higher concentrations of KNO_2 of $1 \cdot 10^{-4}$ to $7.47 \cdot 10^{-4}$ M KNO_2, the more negative wave increased linearly with increasing nitrite concentration, but its half-wave potential remained practically constant in contrast to that for the nitrates.

These experiments demonstrate the advantages of the uranyl method which requires insignificant amounts of uranyl acetate over the lanthanum or cerium methods.

Determination of Nitrates in Pickling Salt

Pickling salts do not contain organic additives (in contrast to salts use for rapid pickling) and should contain, according to State standards [28] only sodium chloride plus 2.00 - 3.70% of potassium nitrate. These mixtures are prepared in refrigerators by mixing the components and the permitted amounts of KNO_3 is not always observed. Apart from the poisonousness of the nitrate itself, there is a possibility of the formation of the even more poisonous nitrites in impermissible amounts during pickling by the action of micro-organisms. It is essential therefore to control the nitrate content both in the solid mixtures used for meat pickling, and in the pickling brine. The uranyl method can be used for nitrate determination in these cases. The supporting electrolyte is 10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ $UO_2(CH_3COO)_2$[1]; to this is added a similar solution which in addition contains 10^{-3} M KNO_3 (Fig. 2), and a calbration curve drawn, the wave height at - 1 V is measured. A 1% solution[2] of pickling salt is then prepared in the above supporting electrolyte and a polarogram taken. Having measured the wave height at - 1 V, the KNO_3 concentration is determined from the calibration curve. If the nitrate content of pickling brine (10 - 25% aqueous solutions of pickling salt) is required, then the brine is diluted 10 times and further additions of standard solution and supporting electrolyte added so that the final concentration of the test solution will be 10^{-2} M with respect to HCl and $2 \cdot 10^{-4}$ M with respect to uranyl acetate.

Determination of Nitrite in Salt for Rapid Pickling "Praganda"

In view of the poisonousness of nitrites it is necessary to ensure a strict control over the nitrites used for rapid pickling, in which the maximum and minimum amounts of sodium nitrite should be 0.6 and 0.5%, respectively. No nitrates can be added to these salts under any circumstances [20, 21].

The uranyl method cannot be used for exact polarographic determination of nitrites in this type of pickling salt (i.e. salts for rapid pickling). The reason for this inapplicability of the uranyl method is the poor reproducibility of the linear relation between concentration of nitrate and height of the nitrite wave, because of the formation of two unknown waves, apparently resulting from the presence of sugars or starches in the pickling salt [23-27].

It was found however that by carrying out the electrolysis in an acetic acid medium the reproducibility of the polarographic wave was good; on passing an inert gas through the solution the wave disappeared completely, thereby showing that it is the result of the reduction of nitric oxide (Fig. 3).

The Nitric Oxide Wave in "Praganda". Curve 1 - 1 ml of 96% acetic acid was added to 9 ml of a 11.1% aqueous solution of "Praganda" after passing nitrogen through the solution; when the resultant solution had been mixed with a glass rod a polarogram was taken starting at 0 V. Curve 2 - The same final solution as for Curve 1 after passing nitrogen through for a short time.

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1) The $2 \cdot 10^{-4}$ M solution contains 0.848 g $UO_2(CH_3COO) \cdot 2H_2O$/liter.

2) The required weighed amount of "Praganda" (a particular type of pickling salt) is taken from a solution of known concentration, the latter being prepared by dissolving at least 10 g of sample.

Curve 3 – the same after passing nitrogen through for a fairly long time. A Kalousk cell was used in conjunction with a saturated calomel electrode, nitrogen was used for sweeping, a 2 V accumulator supplied the voltage and the sensitivity was 1/200.

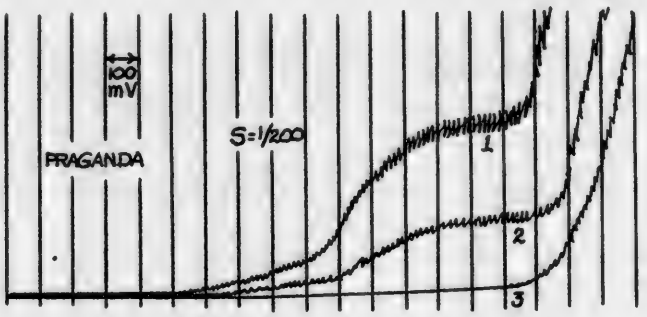

Fig. 3

The following simple method can accordingly be recommended for the polarographic determination of nitrite in salts used for rapid pickling, such as "Praganda".

Solutions. 1) A 10% solution of "Praganda" free from atmospheric oxygen (10 g of solid salt is dissolved in distilled water and made up to 100 ml, the oxygen is expelled beforehand by bubbling nitrogen through it); 2) a standard aqueous solution of 10^{-2} M $NaNO_2$ free from atmospheric oxygen; 3) 10% acetic acid.

Analytical Procedure. 9 ml of 10% acetic acid solution is placed in an electrolytic cell and nitrogen blown through. 1 ml of the 10% solution of "Praganda" free from atmospheric oxygen is then added and the mixture carefully mixed (with a glass rod). Polarograms are taken starting from −0.6 V, using a 2 V accumulator and a sensitivity of ca. 1/100 - 1/500. After recording the curve, ca. 0.5 ml of standard nitrite solution also free from atmospheric oxygen is added, the solution mixed again, and another polarogram taken.

Notes. If nitrites are to be determined in white brine used for rapid pickling (ca. 10 – 20% solution of "Praganda") then the solution can either be placed directly in the electrolytic cell or preliminarily diluted with distilled water free from atmospheric oxygen. Electrolysis is carried out in an inert gas atmosphere, and the mixture carefully mixed after addition of the nitrite so as not to expel the readily volatile nitric oxide. For a large number of determinations the use of a calibration curve is more expedient, while for single determinations the method of standard additions may be used.

An example of how to calculate results from a polarogram when the method of standard additions is used. A standard solution was prepared from 0.0851 g of solid 91.29% $NaNO_2$. Calculated on a basis of 100% $NaNO_2$ this is equivalent to 0.0776 g of $NaNO_2$. This amount was dissolved in distilled water free from oxygen, and the solution diluted to 100 ml. The solution was then 0.0112 M with respect to $NaNO_2$, and 0.5 ml of the solution contained $3.88 \cdot 10^{-4}$ g $NaNO_2$. Calculationn is made by means of the formula

$$x = \frac{hmV}{h'\ (V + a) - hV},$$

where x – is the amount of $NaNO_2$ in g contained in 1 ml of the 10% solution of "Praganda"; h – 29 mm (the height of the wave for weight x of $NaNO_2$; h' – 45 mm (the height of the wave after addition of standard) V – 10 ml

(the volume of the solution being electrolyzed before addition of standard); a – 0.5 ml (the volume of standard added); m – $3.88 \cdot 10^{-4}$ g (the amount of $NaNO_2$ in g in the volume of standard added, a).

Substituting these values in the formula we get $x = 0.616 \cdot 10^{-3}$ g $NaNO_2$. The test sample of "Praganda" therefore contains 0.62% sodium nitrite in the solid state.[1]

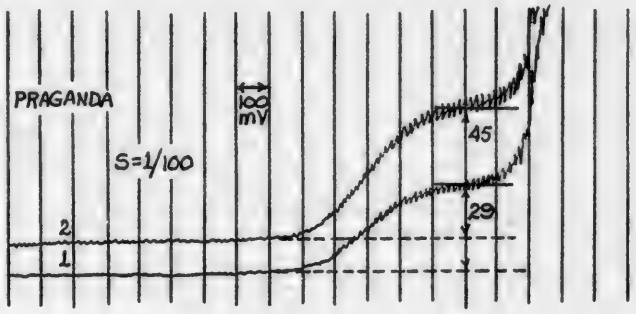

Fig. 4.

Determination of Nitrite in "Praganda".

Curve 1 – to 9 ml of a 10% acetic acid solution through which nitrogen had been passed was added 1 ml of a 10% aqueous solution of "Praganda" free from oxygen, and the solution polarographed, starting at 0 V.

Curve 2 – to the solution with which Curve 1 was taken was added 0.5 ml of 0.0112 M $NaNO_2$ solution free from oxygen. The solution was electrolyzed in a Kalousk cell using a 2 V accumulator and a sensitivity of 1/100; the reference electrode was the saturated calomel electrode.

Determination of Nitrates and Nitrites in Red Brine (Used Brine).

While it is only necessary to determine nitrates (in the brine made from pickling salt) or nitrites (in the brine made from salts used for rapid pickling) in fresh brines (the so called "white" brines, i.e., brines not previously used for pickling), in used brines (the so called red brines) it is necessary to determine both nitrates and nitrites simultaneously. In the course of only 20 days of pickling the salt is under the action of reducing denitrifying bacteria, so that nitrite is formed [20]. On the other hand, in fresh nitrite pickling salt a small amount of the nitrite is converted into nitrate and only after approximately 60 days of pickling do both these salts disappear from the pickling liquid as a result of decomposition by micro organisms and combination of free nitric oxide with hemoglobin to give nitrosohemoglobin [20].

The methods proposed in this article from the polarographic determination of the solid salts used for pickling and for preparing fresh brines are important from the point of view of preventing poisoning which may arise as a result of haphazard and irresponsible methods of preparing the salt mixtures. Determination of nitrates and nitrites in used brine allows one not only to control the pickling process but to regulate it subsequently.

During polarographic investigation of used brines it was shown that even on strong dilution the effect of proteins coming from the meat led to poor reproducibility of the calibration curves when the "uranyl" method was used. This drawback was overcome by precipitating the proteins with alcohol. To 1 ml of used mitrate solution was added 2 ml of ethyl alcohol and the solution left in a test tube on a water bath until most of the protein had been

[1] Chemical analysis of "Praganda" by titration with $KMnO_4$ [22], also showed that this sample contains 0.62% sodium mitrite.

precipitated. The filtrate was diluted with distilled water to approximately 48 ml, 0.5 ml of $2 \cdot 10^{-2}$ M $UO_2(CH_3OO)_2$ was then added and the whole made up with more water to exactly 50 ml. When such a solution is used after adding the usual supporting uranyl electrolyte a linear relation is obtained between concentration and wave height at −1 V (Fig. 5), $E_{1/2}$ is normally shifted to more negative potentials.

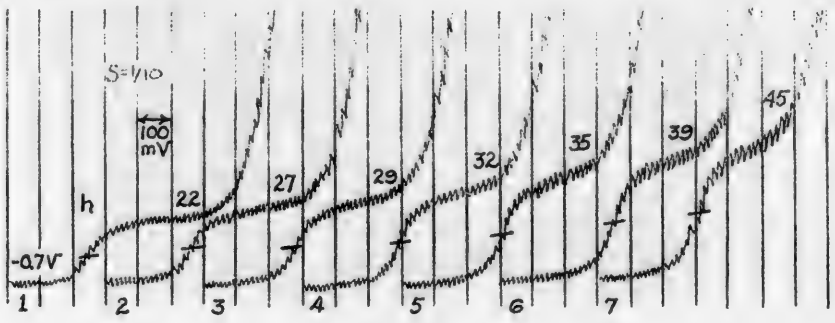

Fig. 5

Nitrate Waves in Used Brine. Curves 1 – 9 were obtained in a uranyl supporting electrolyte (10^{-1} M KCl, 10^{-2} M HCl, $2 \cdot 10^{-4}$ M $UO_2(CH_3COO)_2$; electrolysis was carried out in a nitrogen atmosphere.

Curves 2 – 7 represent what happens when to the solution used for taking Curve 1 was gradually added 0.2 ml lots (1.2 ml altogether) of the solution of used nitrate brine diluted 50 times and partially freed from protein by addition of alcohol; the final solution was $2 \cdot 10^{-4}$ M with respect to $UO_2(CH_3COO)_2$. Polarograms were taken from −0.7 V in a Kalousk cell with a saturated calomel electrode, the voltage was supplied by a 2 V accumulator, in N_2 and the sensitivity was 1/10.

No wave was evident on the polarogram for the brine at −0.7 V (partially freed from NO), consequently this brine did not yet contain nitrite formed by microbe action (this is in agreement with the age of the brine, since it had only been in use for 14 days), the wave at −1 V in Fig. 5 is caused by reduction of nitrates only.

For determining nitrate in brine previously used, electrolysis is carried out in acetic acid medium (as described for "Praganda"); acetic acid precipitates proteins so that there is no need to add alcohol.

After recording the NO wave at −0.7 V, inert gas is passed through the solution to free it from nitrites. Nitrates can then be determined by adding the usual uranyl supporting electrolyte and following the "uranyl" method.

The authors wish to thank the Directors of the Prague Meat Industry, and the "Khmel" factory for gifts of samples of pickling salts and to A. Funfalk of the "Praganda" factory for his valuable discussion of results.

SUMMARY

The authors have tried to modify the polarographic method used for determining nitrates and nitrites in meat pickling salts.

The uranyl method is recommended for analysis of nitrates in pickling salts. In red pickling salts it is necessary to remove protein beforehand by precipitation with alcohol on a water bath. In the case of salts used for rapid pickling the authors determined nitrite in an acetic acid medium on the basis of reduction of the freed nitric oxide. Because of the presence of various organic contaminants (e.g. sugars, starches, etc.) which are added to

the salts for rapid pickling, this determination can be recommended as being a more accurate method than the $KMnO_4$ method.

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413

A STUDY OF THE ERRORS INVOLVED IN THE CHEMICAL ANALYSIS OF STEELS AND CASTS

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Correct evaluation of the errors of chemical analysis is one of the most important factors which decide further improvements in the quality of analytical work. Such an evaluation is only possible by sorting out random from systematic errors of chemical analysis and finding out the contribution of each to the total error. Unfortunately, the importance of this point is underestimated. We aimed at finding out what is the individual importance of systematic and random errors in the errors of chemical analysis, reckoning that if we succeeded then our findings could be used as a basis for recommending improvements.

The most complete information re the evaluation of errors in chemical analysis is obtainable from the results of a large number of analyses carried out in the most highly qualified laboratories. Of interest from this point of view is the material from the archives of the Laboratory of Standard Samples (LSO).

Let us consider briefly what information a study of this material can give us. Investigations of this type should embrace the study of the scattering of results in a series of measurements - by a study of random errors - by comparing the results of analysis of samples with reliable data on the composition of these samples (i.e. by comparison with standards) - and by studying systematic errors. In general, carrying out such an investigation presupposes realization of three conditions: 1) in studying random errors the treated results should actually represent statistically random values; 2) in studying systematic errors the results should not be distorted by superposition of random errors; 3) chemical standards should be available if any decision is to be made as to the existence of systematic errors and as to their size. In practice all these conditions are not completely fulfilled.

Experience has shown that results of chemical analysis of the composition of standard samples and of spectrographic standards cannot be regarded as statistically random and independent, in particular, on account of the fact that the statistical randomness of the results is distorted by the compulsory rejection of some of the results during the process of establishing the chemical composition. It is true to say therefore that the actual scatter of results exceeds that which can be calculated from the material available in the analytical archives.

The second condition, although it can only be satisfied to a limited extent, nevertheless can be satisfied to an extent sufficient to ensure good enough accuracy when special methods of calculation are employed.

If the third condition is to be fulfilled, then, strictly speaking, it is essential to know the true composition of the test material, this is of course impossible. One must, therefore, replace comparison with standards the results of which are known to be reasonably accurate, by a comparison with standards the composition of which are only known to various degrees of approximation. As an arbitrary standard, for want of a better one, it is possible to use the mean content of an element in a standard sample (or spectrographic standard) as established from the results of all the analysts.

Thus, the values of random and systematic errors of chemical analysis, which are obtained by treating test material similar to that of the analytical archives of the Laboratory of Standard Samples, should be considered as values established with a definite approximation.

An attempt to treat such material was made by Groshev and Ponosov [1]. These authors assumed that in chemical analysis there exist some systematic errors which do change under any circumstances but are innate in the method itself (method error), and systematic errors which are innate in a given series of measurements and which arise as a result of factors unrelated to the nature of the method. In their investigations only method errors were studied, so that they did not give a complete picture of the value of systematic errors. Practice shows that results of analysis carried out in different laboratories even when the same method is used, often exhibit a systematic deviation. This testifies to the important part played by systematic errors which are not related to the nature of the method. It is therefore more correct to use the term systematic analytical error in the sense of a constant error inherent in a given series of measurements of chemical composition carried out by an analyst or laboratory, and not only in the sense of an "error in method" or a "constant value" as if it were a characteristic of a given analyst or laboratory in general, irrespective of the test material analyzed.

In preparing the original results for calculation the authors of the article indicated [1], evaluated the compatibility (as a member of one statistical series) or incompatibility of the measurements of two analysts by the Student-Fisher Test [2], in which they exclude obviously incompatible results, and assumed that the difference in the averages compared in the remaining instances was random assumed united into one statistical series. Nevertheless a large number of measurements not excluded by these authors could contain values which very often vary to a considerable extent, in addition to the random and systematic errors which are inherent in one or another group of results, although it would be impossible to establish these reliably because of the significant uncertainty in the values found for the dispersion when dealing with a small number of measurements (4-6 for each of the dispersions compared in evaluating the compatibility of the measurements made by two analysts; 8-12 for evaluating the measurements of two laboratories). Moreover the case is possible where both sets of measurements being compared have a common systematic error.

We carried out a statistical treatment of material available in the analytical archives of the LSO, in which we took into account the deficiencies of the previous work (some of the original material used for calculation and obtained by the authors of [1] was used for this purpose). Material obtained on the analysis of standard samples and spectrographic standards for simple and multicomponent steels and casts were treated.

The following method of calculation was used for determining the value of the random errors in chemical analysis. In order to eliminate the effect of hidden systematic errors, the dispersions were calculated from the results obtained by each analyst separately, and not from all the mass of material taken as a whole. Each of the values found in the way for the dispersion σ_i^2 as a result of treating a small number of measurements was not reliable enough. Nevertheless the mean value of the dispersion

$$\sigma^2_{\text{av.}} = \frac{\sum \sigma_i^2}{n}$$

where n – the number of analysts participating in the analysis of a given standard sample or spectrographic standard (usually 16-20), characterizes the accuracy of the determination considerably more reliably. By using this technique it is possible to exclude not only the effect of hidden systematic errors inherent in the results of various laboratories but also to exclude the effect of hidden systematic errors inherent in the results of different analysts

even though working in the same laboratory. Using the mean values found for the dispersion, calculations were made of the corresponding mean square errors which were expressed in relative percentages (in all 6000 measurements were dealt with). The relations established between the values determined for the contents of various elements and the value of the mean square errors are adduced in Fig. 1.[1)]

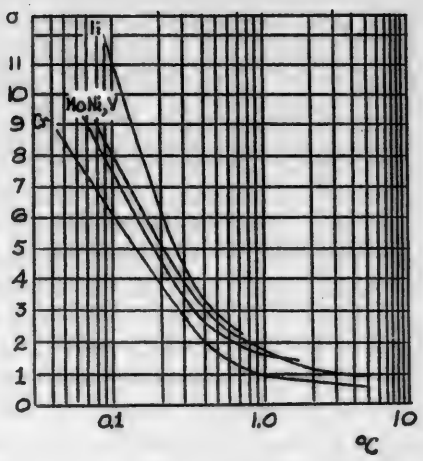

Fig. 1. Change in value of the random error (mean square error of a " single measurement") of chemical analysis of steels and casts with the value of the content of the element determined (the value of the error is expressed in relative %).

Evaluation of the systematic errors of chemical analysis is incomparably more difficult since the true contents of the test elements are unknown. If, arbitrarily, in the absence of information as to the true composition, one should start off with the average content established from the mean results of all the analysts for a given standard sample or spectrographic standard, then one can take the deviation of the mean results for each laboratory (mean of 8-10 determinationsby each method) from the calculated overall mean as the value of the systematic error.

The relation between the systematic errors calculated in this way and the value of the contents determined for the elements is adduced in Fig. 2. (results of treating ca. 1200 means). It is pertinent to point out that the curves adduced in Figs. 1 and 2 reflect only the mean values of the errors, while at the same time one very often comes up against considerable deviations from the means.

The results adduced show that the values of the systematic and random errors are of the same order, even when carrying out such responsible work as the chemical analysis of standard and spectrographic standards.

When measuring the results of several meansurements, if the value of the random error of a result decreases then the specific contribution of the systematic errors correspondingly increases. This is observed in particular also when comparing the results of several laboratories determining the composition of standard samples and spectrographic standards: in many cases the results of each laboratory are grouped round its mean, but the mean, despite averaging, still differs from one laboratory to the other.

When, in addition to what has already been said, one takes into account that metrological requirements for the exclusion of systematic errors are incomparably more strict than for random errors [3], then it is true to say that the question of controlling systematic errors has a significance for analytical practice which is at least as great, if not of greater, importance than the question of controlling random errors.

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1) The curves given in Figs. 1 and 2 were constructed from results obtained for all the methods of chemical analysis employed, since it had not been established that any particular method gave any essential different accuracy or reliability from other methods used for the chemical analysis of standard samples or spectrographic standards.

The sole effective means of controlling systematic errors in analysis is the use of standard samples since the results of their chemical analysis are considerably freer from systematic and random errors than results obtained in any individual laboratory. The use of All-Union standards in industrial and research laboratories would signify the unification of control of the correctness of the results of chemical and spectrographic analysis on the basis of introducing more reliable measures. Nevertheless, the question of how to deal with systematic errors is not touched upon in any GOST methods, nor has the use of standard samples and spectrographic standards for the control of analytical results been specified. Meanwhile, the results obtained do show that in considering the question of analytical errors proper attention must be paid not only to the evaluation and control of random error but also to the evaluation and control of systematic errors. Such an evaluation and control should be carried out by analyzing standard samples and spectrographic standards similar in composition and properties to the test sample. When this is done it is essential to ensure the necessary accuracy of the test results obtained (to eliminate random errors). The permitted values of the deviation of the mean result obtained from the certified results of the standard samples and spectrographic standards should be established, taking into account the acceptable values of the systematic errors and the accuracy of the mean results obtained.

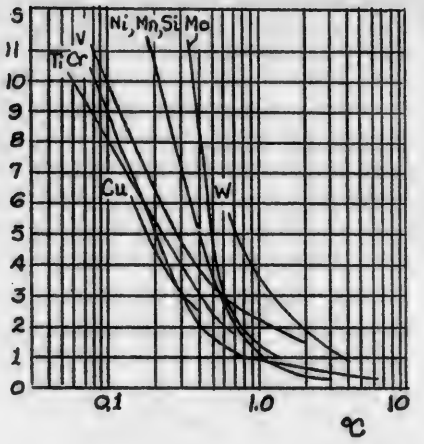

Fig.2. Change in the value of the systematic error in the chemical analysis of steels and casts with the value of the determined content of the elements (the value of the error is expressed in relative percentages.)

SUMMARY

Systematic and random errors arising during chemical analyses of standard samples and spectrographic standards of steels and casts have been studied separately. It has been shown that the systematic errors which arise during chemical analysis are of the same order of magnitude as random errors of single measurements and exceed the random errors of results obtained by averaging several measurements. In this connection the importance of using All-Union standard samples for controlling systematic errors is emphasized.

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C R I T I C I S M

A. I. Busev. The Analytical Chemistry of Bismuth. Acad. Sci. USSR press, Moscow, 1953, pp. 382, 100 Tables containing numerical data. Bibliography of 1396 references. Printing 2000. Price 21 rubles.

A.I. Busev's book is the first monograph in Soviet chemical literature to be devoted to an overall survey and critical exposition of the method used for detecting and determining bismuth in its compounds and in products of various origins. The most worthy feature of the book is the clear and logical way it is set out. The author divides his book into seven chapters which are based on the types of reactions characteristic of bismuth ions. The first chapter is devoted to the hydrolysis reactions of bismuth compounds; some of the reactions were already known during the XVI century. The practical use of these hydrolysis reactions for qualitative and quantitative analyses relates to the beginning of the last century. Further improvements were made to hydrolysis methods recently. Instead of water, alkali hydroxides, or carbonates, which were used in the past, the tendency now is to use materials exhibiting buffer action for hydrolyzing bismuth salts materials such as: urotropine, pyridine, sodium formate, sodium nitrite, ammonium carbonate, etc. The basic bismuth salts which are formed on hydrolysis such as BiOCl, BiOBr and $(BiO)_2CO_3$, can be used for the gravimetric determination of this element. The accuracy of methods based on hyrolysis is not very good, but is nevertheless good enough for technical analysis of ores, alloys, and also of pharmaceuticals.

The methods proposed by P. P. Solodovnikov are successful examples of these methods. The method of coprecipitation developed by N.A. Tananaev and coworkers is of special importance for the separation of bismuth from other heavy metals and for the detection of bismuth.

The author of this book has paid little attention to preventing hydrolysis of bismuth salt solutions. This problem which is not only of analytical importance but also of biological significance has been studied by Turkevich [1]. New light has been thrown on the composition of bismuth tartrate complexes in the published papers of Tsimbler [2], and Tikhonov [3].

In the following chapter the reactions of bismuth with inorganic anions are discussed. Most gravimetric determinations of bismuth are based on the formation of the sulfide, phosphate, arsenite, bichromate, hexathiocyanochromate, and other sparingly soluble compounds of this metal. The detailed study of the properties of bismuth sulfide is of special importance. Determination of the solubility product carried out by A.F. Kapustinsky, and also the position occupied in the solubility series of the metal sulfides, as pointed out by N.A. Tananaev, permit one to forecast the behavior of bismuth ions during analysis.

The formation of the acid-stable phosphate $BiPO_4$ is used at present not only for the analysis of bismuth but also for the determination of phosphoric acid.

Valuable information is given in this section on the determination of bismuth in its organic compounds, and also in biologically important materials.

The separation of bismuth from the other metals of the hydrogen sulfide group, such as mercury, lead, thallium, cannot be regarded as fully worked out. A careful study of the physico-chemical reaction conditions will undoubtedly lead to further improvements in these difficult determinations.

The next chapter deals with the reactions which occur between bismuth and organic molecules. The use of organic reagents in analytical chemistry, which

was proposed at the beginning of this century by L.A. Chugaev, is of great importance also for bismuth. The thiourea complexes of bismuth, which have been known for 50 years, find application for the qualitative detection and colorimetric determination of this metal.

A number of sulfur-containing compounds are used in the analytical chemistry of bismuth, among these are; diphenylthiocarbazide, dithizone, captax, thionalide, and many others. Thionalide still remains the most convenient reagent for detection and determination of bismuth. The use of dithizone ensures high sensitivity. The worst feature of this method is the necessity of using CCl_4 or $CHCl_3$ as solvents.

Phenols constitute the second large group of organic compounds which give characteristic compounds with Bi^{3+} ions; among these mention should be made of pyrogallol, gallic acid, and also oxine.

Complexone III (Trilon B) has very recently been suggested for determination of bismuth; the sodium salt of ethylenediaminetetracetic acid in the presence of a special indicator -pyrocatechinsulfonphthalein- this method has been suggested in the works of Malat, Suk, and Ryba [4].

The fourth chapter of the monograph deals with all the numerous complex halides of bismuth which usually contain organic bases as well. The iodide derivatives of bismuth which contain the ions: $[BiI_4]^-$, $[BiI_5]^{2-}$, $[BiI_6]^{3-}$, $[Bi_2OI_9]^{3-}$, etc., are of utmost importance in analytical practice.

In the case of complex bases the iodo- bismuth reactions are not so much used for the detection of bismuth as for the identification of the base or alkaloid itself. Reactions with quinine, cinchonine, brucine, caffeine, cocaine, strychnine, narceine, and other alkaloids, which were first studied by Dragendorf [5], are of this type.

The thiocyanate complexes of bismuth are similar in character to the halides. Thanks to the work of the Yu.Yu.Lurye, A.K. Babko, and I.M. Korenman, colorimetric methods have been developed for bismuth with sensitivities down to 0.1 γ/ml.

The subsequent section of the book is devoted to reactions which occur at high temperatures, chiefly in the dry state. The title heading: "Some reactions which occur without a change in the valency of bismuth" does not really demonstrate what the reactions have in common.

The behavior of bismuth oxide and bismuth sulfide at high temperatures, and also results on the volatility of the bismuth halides, are of exceptional importance for the analytical determination of this element. This is confirmed by the work of the French chemists Panchout and Duval [6], which was published after the present book was written; their paper "Thermogravity of organic precipitates" No. XLVII contains results on 36 bismuth compounds. Busev should expand this chapter in future editions.

Oxidation-reduction reactions of bismuth compounds are considered in chapter 6. Reduction of bismuth to metal by means of various reducing agents is the most important in this connection.

Exceptionally good results were obtained by Busev when he used chromium dichloride as reducing agent. $TiCl_3$, $SnCl_2$, $VOSO_4$, H_3PO_2, $Na_2S_2O_4$ etc. have been successfully used in acid media. Reduction reactions can also be carried out in alkaline media by using sodium stannite, formaldehyde, glucose, and complex manganese and nickel cyanides as reducing agents. Replacement of bismuth electrochemically by other metals is also used. Of interest from a theoretical point of view, although it has not been studied sufficiently, is the reaction: $3Cu + 2Bi^{3+} \longrightarrow 2Bi + 3Cu^{2+}$, which follows different paths according to the presence of complexing ions, pH, and rH of the medium, and other experimental conditions. Oxidation of bismuth to higher valencies followed by reduction

is not quantitative and is therefore of little significance in analytical chemistry.

The last chapter is devoted to physico-chemical methods of detecting and determining bismuth. This chapter includes brief reviews of the following methods: flame coloration, quantitative spectrographic analysis, X-ray analysis, and also the marked atoms method. A. Busev's review in 'Progress of Chemistry, [7] leads us to suggest that the author should supplement this section of his outstanding monograph.

The bibliography is exceptionally well worked out and embraces 1396 references, covering the period from the beginning of the last century to 1951.

One of the drawbacks of the book is the absence of an author index, so that one cannot look up papers by a particular author in the text. The few mistakes in the book do not lower the overall importance of this book as a contribution not only to Soviet but to world chemical literature.

The success of this monograph on the analytical chemistry of bismuth should serve as an impetus for extending this idea to other elements.

Lvov

August 31, 1954

K.N. Mikhalevich
N.M. Turkevich
L.I. Panteleeva

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1) See Consultants Bureau Translation, p. 33.

DMITRII IVANOVICH RYABCHIKOV

(On his fiftieth birthday)

On the 6th of November Dmitri Ivanovich Ryabchikov, one of our foremost chemists - a doctor of chemical sciences, a professor, and a Stalin prize winner - celebrated his 50th birthday.

Dmitri Ivanovich, a pupil of N.S. Kurnakov, is well known as a scientist fruitfully working in the fields of theoretical and practical inorganic and analytical chemistry on problems connected with the study and analysis of the rare and noble metals.

Ryabchikov finished in the Technical Department of the Plekhanov Moscow Institute of Natural Economy in 1931.

After finishing in the Institute he became a candidate for a degree in the Institute of General and Inorganic Chemistry, Acad. Sci., USSR, and in 1934 defended his thesis on the "Strength of Isomeric Bases" which he carried out under the direction of Corresponding Member of the Academy of Sciences A.A. Greenberg.

While a coworker at the Institute of General and Inorganic Chemistry Ryabchikov headed a number of expeditions to study salt deposits.

Under the direction of Academician N.S. Kurnakov he studied the potassium-magnesium deposits of the sulfate type in various parts of the Soviet Union. He showed that certain minerals contained potassium. He also demonstrated the high efficiency possible by using mixed potassium sulfates as fertilizers.

He also carried out work on the stereochemistry and physical chemistry of noble metal complex compounds. He was the first to characterize the large class of the thiosulfate compounds of platinum, palladium, silver, gold, and of other elements.

Many of the complex compounds which he synthesized (over 50) contained a complex ion with six charges, which is something new in the chemistry of complex compounds. The thiosulfate compounds are more stable than any hitherto known.

The thiosulfate "Ryabchikov reaction" is one of the most reliable means of determining the isomeric character of complex compounds. He also carried out work on the stereochemistry of complex compounds along other lines, in particular, he prepared and characterized the little-studied class of the sulfite complex compounds (e.g. $Na_2[Pt(SO_3)_2(NH_3)_2]$, $Na[Pt(Tham)_2\ (SO_3)_2]$, etc. He showed that SO_3^{2-} is a vigorous complexing agent and is comparable with thiosulfate and thiourea.

Ryabchikov was the first to establish that in complex compounds there is a relation between strength and isomeric character. Of exceptional importance is the work he did on the application of electrometric titration for solving a number of problems connected with a study of the structure of the inner sphere of complex compounds.

His work on the mechanism of oxidation of platinum thiosulfate compounds by potassium bromate, in which he used potentiometric titration, is very interesting. This method permits determination of the instability constants of many complex platinum compounds, and on the basis of the results it is possible to solve the question of the polarization of complex molecular compounds.

By studying the thiosulfate compounds of silver – $Na_3[Ag(S_2O_3)_2]$, $Na_4[Ag_2(S_2O_3)_3]$ – he showed that silver can occur not only in the inner but also in the outer sphere of the complex, depending on the concentration of the reactants, e.g. $AgNa_2[Ag(S_2O_3)_2]$.

These researches on the thiosulfate compounds of platinum and other metals were made the basis of his thesis for his doctorate, which he defended in 1942.

The development of theoretical studies on complex compounds served as a basis for working out analytical methods. Potentiometric and colorimetric methods were particularly widely used.

In the analytical chemistry of the platinum metals (Pt, Ir, Rh, Os and Au) Ryabchikov developed original methods of detecting individual metals and analyzing alloys, and industrial intermediates. These methods are used in control work; e.g. cerimetric determination of lead, or the colorimetric determination of rhodium in the presence of platinum, etc.

Ryabchikov has been devoting his time recently to the elements of the rare-earth group. In this hitherto little-studied branch of inorganic chemistry he has successfully applied the teachings of the Chugaev school.

New complex compounds of elements of this groups have been isolated by Ryabchikov. It has been established that these elements are specific complexing agents which differ essentially from many other heavy elements. Being quadrivalent they have a coordination number of "six". Rare-earth ions do not form non-ionic bonds with the majority of the usual coordinating substituents, even such vigorous ones as the thiosulfate, iodate and nitrite ions etc; on the other hand, organic amines which contain a tertiary nitrogen form complex compounds of average stability.

The coordination bond in this group of metals is best formed through an oxygen atom to carbonates, sulfates and other inorganic acids, and particularly with organic acids containing a few carboxyl groups. A vast amount of information has been collected on complex formation between rare earths and carboxylic acids, monobasic, dibasic, and tribasic hydroxy acids, mono- and multi-basic amino acids, and sulfonic acids of the benzene, naphthalene, and anthracene series. It has been established that the combination in an organic molecule of three carboxylic groups (nitrile, triacetates, citrates) ensures the formation of very stable complex ions.

Isomeric compounds of this type have been prepared, e.g. for praseodymium and neodymium; they alternately enter the inner and outer spheres.

One of the characteristic features of the complex compounds of the rare-earths is extreme sensitivity to change of medium; increasing the acidity of their solutions leads to weakening of the coordination bond and a switch to an ionic state.

The work being carried out in the laboratory of the Vernadsky Institute of Geochemistry and Analytical Chemistry under the direction of Ryabchikov on analysis, isolation, and preparation of the rare-earths from natural minerals by chemical and chromotographic methods is an essential contribution to the chemistry of the rare-earths.

A note may be given here of a new sensitive reaction and a colorimetric method for determination of cerium which are based on the formation of a citrate complex $Na_5[Ce(C_6H_5O_7)_3]$ with hydrogen peroxide in alkaline media.

During a study of the thiosulfate complexes of certain rare-earths, Ryabchikov isolated new compounds in alcoholic media and clarified the mechanism of interaction between quadrivalent cerium and thiosulfate.

Ryabchikov and his coworkers have made a concerted attack on the possibilities of using ion-exchange resins in analytical chemistry, in particular for the separation of rare-earths and some others, and also for the preparation of inorganic compounds in a very pure state.

The theory which he has developed re the chemical nature of ion exchange processes has found recognition among research workers in the field of chromatography, and has opened up ways of synthesizing resins with selective action. Under his direction a valuable comparative study of Russian synthetic ion-exchange resins has been made. Analytical methods involving the use of ion-exchange materials have been proposed, e.g. determination of copper and iron in alloys, in which differences in the stability of phosphate and ammonium complexes are used; determination of rhenium in molybdenum concentrates, etc.

All Ryabchikov's scientific activity has been indissolubly linked with teaching. For 20 years he has been teaching chemistry in the Moscow Region Teaching Institutes and has held the chair there. During his time he has taught numerous cadres of chemists in intermediate schools and his teaching experience has been incorporated in a text book of chemistry.

His research students work on the chemistry of the complex compounds of the rare-earths and on chromatographic analysis.

He is also in close touch with industrial and factory laboratories, and acts as a scientific consultant on various questions of production control.

His organizing activity as a deputy director of the Vernadsky Institute is also worthy of note, he has devoted much time and energy to developing the analytical section of this Institute. Being a deputy chairman of the Commission on Analytical Chemistry, he has striven to improve industrial production of chemical reagents and apparatus; in addition he has been instrumental in calling scientific conferences on analytical chemistry.

From its inception, Ryabchikov has been secretary to the board of "J. Anal. Chem." and also the editor of several papers and monographs.

The government value his services highly. He has been awarded a Stalin prize. He has also been awarded the orders of Lenin, and the Red Banner, and a Badge of Honor.

He is well liked and honored by a wide circle of analysts.

In celebrating his birthday his numerous pupils, coworkers and friends wish him the best of health, and hope that he will gain further successes in developing analytical chemistry for the benefit of our country.

NINTH CONFERENCE ON SPECTROSCOPY

The 9th conference on spectroscopy which was held at Tartu in the Estonian Republic from the 5th to the 11th of July, was attended by 700 representatives of scientific research institutes, higher education establishments, and factories from various parts of the Soviet Union.

One hundred and eighty five papers were read at the conference, of which 53 were devoted to molecular spectroscopy, while the others were devoted to studies of atomic spectra, to processes occurring at the excitation source, spectrographic apparatus, and spectrographic methods of analyzing various products.

Fifteen reports were concerned with descriptions of new apparatus made in Russia and indicated considerable achievements in the production of spectrographic equipment.

The first spectrographs with diffraction gratings to be put into production were the flat (DSF-3) and curved (DFS-2) types. These instruments are distinguished by high linear dispersion – 2A/mm to 4A/mm (in the first order) and a high resolving power – 100,000-150,000. The diffraction gratings are modern and as good as foreign makes.

The three prism spectrograph, the ISP-67, with a resolving capacity of 150.000, is of the class which has a high dispersion; this instrument is also characterized by high candlepower, whereby the superfine structure of mercury can be observed. Two other spectrographs have also been issued: the ISP-66 (similar to the ISP-22) with a mirror collimator (parabolic mirror) which can be used for observing weak fluorescence; the super candle power spectrograph (ISP-63) which has large prisms is suitable for expedition conditions; with this instrument the illumination of the night sky can be investigated. Vacuum instruments of three types have been developed by our industry: 1) with a bent diffraction grating which permits spectra in the extreme ultraviolet to be obtained; 2) a vacuum fluorite tube with which it is possible to observe spectra up to 1200 A; and 3) a vacuum monochromator (up to 1300-1400°) with a fluorite optic and a photo-electric set-up.

A beginning has been made in production of attachments for the ISP-51 spectrophotometer with a photomultiplier, an amplifier, and a recording attachment. The IKS-11 and IKS-6 for study in the infrared have also been issued, as well as the spectrophotometers SF-4 and SF-2M. For visual observation the following have been prepared: the SL-10 styloscope, the ST-7 stylometer, a manual spectroscope, and a demonstration outfit; new apparatus for measuring spectrograms have also been turned out.

A number of reports were devoted to photoelectric methods which speed up analysis and make it more accurate. Considerable attention was given to impulse sources of excitation, which have several advantages in a number of applications.

Results of study of the processes which occur in the flame of an excitation source and on the electrodes were given in 15 reports. These processes have received little attention so far, although they have a significant effect on the analytical results; these papers were therefore of exceptional value.

Seventy reports touched upon spectrographic analysis of various products; metals, slags, various mineral raw materials, solutions, natural waters,

electrolytic baths, lubricating oils, etc. Methods for detecting small amounts of contamination in metals of high purity (titanium, vanadium, zinc, antimony) were also described.

Papers on the spectrographic determination of hydrogen and oxygen in metals proved of great interest. Mention must also be made of the application of emission spectrographic analysis in biology and medicine as described in papers devoted to the study of the biological role of micro-elements.

Reports were also heard on the following topics: 1) the contemporary study of radiospectroscopy, and 2) the determination of molecular structure by radiospectroscopy.

The conference enabled many scientists in the field of spectroscopy to exchange views and to get acquainted with new apparatus and methods, new techniques and improvements, so it should prove of great help in ensuring successful continuation of work in this field.

T. Borovik-Romanova

TRANSLATION TO AND FROM ALL LANGUAGES

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